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Fresenius

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A
SYSTEM OF INSTRUCTION
IN
QUANTITATIVE CHEMICAL ANALYSIS.

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IN
QUANTITATIVE CHEMICAL ANALYSIS.

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SAMUEL W. [illegible] SON, M.A.,

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EDITOR'S PREFACE.

In preparing this edition of Fresenius' Quantitative Chemical Analysis, the editor has sought by various changes to adapt it to the wants of the American student.

The foreign editions have attained such encyclopedic dimensions as to occasion the beginner no little confusion and embarrassment. For this reason the bulk of the work has been considerably reduced. A few processes which the editor's experience has convinced him are untrustworthy, and many more that can well be spared because they are tedious or unnecessary, have been omitted. The entire chapter on Analysis of Mineral Waters, excellent as it is, has been suppressed on account of its length, and because the few who have occasion to make detailed investigations in that direction have access to the original sources of information.

The section on Organic Analysis has been reduced from sixty to thirty pages, mainly by the omission of processes which from their antiquity or inferiority are more curious than useful. The chapters on Acidimetry and Alkalimetry have been likewise greatly condensed, and all that especially relates to Soils and Ashes of Plants has been left out. The recent appearance of an excellent special treatise on "Agricultural Chemical Analysis," by Professor Caldwell, of Cornell University, justifies the last-named omission.

On the other hand, some important matter has been added. Bunsen's invaluable new methods of treating precipitates are described in his own (translated) words. Various new methods of estimation and separation are incorporated in their proper places.

The editor thankfully acknowledges his indebtedness to several gentlemen for special contributions to this work; viz.: To Dr. J. Lawrence Smith, who has kindly furnished a manuscript account of his admirable method of fluxing silicates for the estimation of alkalies. To O. D. Allen, Esq., late chemist to the Freedom Iron

Works, Lewistown, Pennsylvania, for copious notes of his extensive experience in the analyses of steel, iron, and iron ores, which have been freely employed in §229. To Mr. Wm. G. Mixter, chief assistant in the Sheffield Laboratory, for the account of the gold and silver assay. To Professor Brush, of Yale College, Professor Collier, of Vermont University, and B. S. Burton, Esq., of Philadelphia, for various important facts and suggestions. Just before going to press, Dr. Wolcott Gibbs has communicated an account of his new method of finding at once the total correction for temperature, pressure and moisture in absolute determinations of nitrogen or other gases, which, from its simplicity, convenience, and accuracy must prove of the highest service to chemistry. It will be found, with some other matters,* in an appendix, p. 619.

The additions which have been made to the methods of examining ores, it is believed, adapt the work to meet all the ordinary requirements of the metallurgical and mining student.

The editor's additions are distinguished, in all important cases, by enclosure in brackets, [ ].

While fully recognizing the necessity of teaching the new notation and nomenclature of chemistry, the editor has in this book retained the old system, because it is identified with the chemical literature of the century, and cannot be speedily forgotten by practical men. At a time when the most elementary text-books are framed on the "modern" system, it is important to keep the student exercised in the language of the old masters of the science, which is still, and must for some time remain, a part of the vernacular of the physician, the apothecary, the metallurgist, and the manufacturer.

SAMUEL W. JOHNSON.

SHEFFIELD LABORATORY OF YALE COLLEGE, Dec., 1869.

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* Viz., assay of chrome iron, and separation of phosphoric acid from lime, alumina, and iron.

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INTRODUCTION.

As we have already seen in the "Manual of Qualitative Analysis,"—to which the present work may be regarded as the sequel,—Chemical Analysis comprises two branches, viz.: *qualitative analysis* and *quantitative analysis*, the object of the former being to ascertain the *nature*, that of the latter to determine the *amount*, of the several component parts of any compound.

By QUALITATIVE ANALYSIS we convert the *unknown* constituents of a body into certain *known* forms or combinations; and we are thus enabled to draw correct inferences respecting the nature of these unknown constituents. Quantitative analysis attains its object, according to circumstances, often by very different ways; the two methods most widely differing from each other, are *analysis by weight*, or *gravimetric analysis*, and *analysis by measure*, or *volumetric analysis*.

GRAVIMETRIC ANALYSIS has for its object to convert the *known* constituents of a substance into forms or combinations which will admit of the most exact determination of their weight, and of which, moreover, the composition is accurately known. These new forms or combinations may be either *educts* from the analyzed substance, or they may be *products*. In the former case the ascertained weight of the eliminated substance is the direct expression of the amount in which it existed in the compound under examination; whilst in the latter case, that is, when we have to deal with *products*, the quantity in which the eliminated constituent was originally present in the analyzed compound, has to be deduced by calculation from the quantity in which it exists in its new combination.

The following example will serve to illustrate these points:—Suppose we wish to determine the quantity of mercury contained in the chloride of that metal; now, we may do this, either by precipitating the metallic mercury from the solution of the chloride, say by means of protochloride of tin; or we may attain our object by precipitating the solution by sulphuretted hydrogen, and weighing the precipitated sulphide of mercury. 100 parts of chloride of mercury consist of 73·82 of mercury and 26·18 of chlorine; consequently, if the process is conducted with absolute accuracy, the precipitation of 100 parts of chloride of mercury by protochloride of tin will yield 73·82 parts of metallic mercury. With equally exact manipulation the other method yields 85·634 parts of sulphide of mercury.

Now, in the former case we find the number 73·82 directly; in the latter case we have to deduce it by calculation:—(100 parts of sulphide of mercury contain 92·593 parts of mercury; how much mercury do 85·634 parts contain?

100 : 85·634 :: 92·593 : x = 79·291

As already stated, it is absolutely indispensable that the forms into which bodies are converted for the purpose of estimation by weight should fulfil two conditions: first, they must be capable of being weighed exactly; secondly, they must be of known composition.—for it is quite obvious, on the one hand, that accurate quantitative analysis must be altogether impossible if the substance the quantity of which it is intended to ascertain, does not admit of correct weighing; and on the other hand, it is equally evident that if we do not know the exact composition of a new product, we lack the necessary basis of our calculation.

Volumetric analysis is based upon a very different principle from that of gravimetric analysis; viz., it effects the quantitative determination of a body, by converting it from a certain definite state to another equally definite state, by means of a fluid of accurately known power of action, and under circumstances which permit the analyst to mark with rigorous precision the exact point when the conversion is accomplished. The following example will serve to illustrate the principle of this method:—Permanganate of potassa added to a solution of sulphate of protoxide of iron, acidified with sulphuric acid, immediately converts the protoxide of iron to sesquioxide; the permanganic acid, which is characterized by its intense color, yielding up oxygen and changing to protoxide of manganese, which combines with the sulphuric acid present, to colorless sulphate of protoxide of manganese. If, therefore, to an acidified fluid containing protoxide of iron, we add, drop by drop, a solution of permanganate of potassa, its red color continues for some time to disappear upon stirring; but at last a point is reached when the coloration imparted to the fluid by the last drop added remains: this point marks the termination of the conversion of the protoxide of iron to sesquioxide.

Now, by accurately determining the strength or power of action of the solution of permanganate of potassa—which is done simply by making it act upon a known quantity of protoxide of iron in solution, and correctly noting how much of it is required to effect the conversion of that protoxide to the state of sesquioxide—we are now able with this solution to determine the exact amount of protoxide of iron present in any solution. Thus, we will assume, for instance, that we have found it takes exactly 100 parts of our solution of permanganate of potassa to oxidize 2 parts of protoxide of iron; if now, in testing, with this standard solution of permanganate of potassa, any solution containing an unknown quantity of protoxide of iron, we find that 100 parts of our standard fluid are required to oxidize the iron, we know at once that the examined fluid contained exactly 2 parts of protoxide of iron; if 50 parts are required, we know that 1 part of protoxide of iron was present, &c. &c. Accordingly, by simply measuring the quantity used of our standard solution of permanganate of potassa, we arrive at once at an accurate knowledge of the amount of protoxide of iron.

As the process of measuring is mostly adopted, in preference to that of weighing, for determining the quantity used of the standard fluid, we give to this analytical method the name of "analysis by measure." It generally leads to the attainment of the object in view with much greater expedition than is the case with analysis by weight.

To this brief intimation of the general purport and object of quantitative analysis, and the general mode of proceeding in analytical researches, I have to add that certain qualifications are essential to those who would devote themselves successfully to the pursuit of this branch. These qualifications are, 1, theoretical knowledge; 2, skill in manipulation; and 3, strict conscientiousness.

The preliminary *knowledge* required consists in an acquaintance with qualitative analysis, the stoïchiometric laws, and simple arithmetic. Thus prepared, we shall understand the method by which bodies are separated and determined, and we shall be in a position to perform our calculations, by which, on the one hand, the formulæ of compounds are deduced from the analytical results, and, on the other hand, the correctness of the adopted methods is tested, and the results obtained are controlled. To this *knowledge* must be joined the *ability of performing the necessary practical operations.* This axiom generally holds good for all applied sciences, but if it is true of one more than another, quantitative analysis is that one. The most extensive and solid theoretical acquirements will not enable us, for instance, to determine the amount of common salt present in a solution, if we are without the requisite dexterity to transfer a fluid from one vessel to another without the smallest loss by spirting, running down the side, &c. The various operations of quantitative analysis demand great aptitude and manual skill, which can be acquired only by practice. But even the possession of the greatest practical skill in manipulation, joined to a thorough theoretical knowledge, will still prove insufficent to insure a successful pursuit of quantitative researches, unless also combined with *a sincere love of truth, and a firm determination to accept none but thoroughly confirmed results.*

Every one who has been engaged in quantitative analysis knows that cases will sometimes occur, especially when commencing the study, in which doubts may be entertained as to whether the result will turn out correct, or in which even the operator is *positively convinced* that it *cannot* be *quite* correct. Thus, for instance, a small portion of the substance under investigation may be spilled; or some of it lost by decrepitation; or the analyst may have reason to doubt the accuracy of his weighing; or it may happen that two analyses of the same substance do not exactly agree. In all such cases it is indispensable that the operator should be conscientious enough to repeat the whole process over again. He who is not possessed of this self-command—who shirks trouble where truth is at stake—who would be satisfied with mere assumptions and guesswork, where the attainment of positive certainty is the object, must be pronounced just as deficient in the necessary qualifications for quantitative analytical researches as he who is wanting in knowledge or skill. He, therefore, who cannot fully trust his work—who cannot swear to the correctness of his results, may indeed occupy himself with quantitative analysis by way of practice, but he ought on no account to publish or use his results as if they were positive, since such proceeding could not conduce to his own advantage, and would certainly be mischievous as regards the science.

The domain of quantitative analysis may be said to extend over all matter—that is, in other words, anything corporeal may become the object of quantitative investigation. The present work, however, is intended to embrace only the substances used in pharmacy, arts, trades, and agriculture.

Quantitative analysis may be subdivided into two branches, viz., analysis of *mixtures*, and analysis of *chemical compounds*. This division may appear at first sight of very small moment, yet it is necessary that we should establish and maintain it, if we would form a clear conception of the value and utility of quantitative research. The quantitative analysis of mixtures, too, has not the same aim as that of chemical compounds; and the method applied to secure the correctness of the results in the former case is different from that adopted in the latter. The quantitative analysis of chemical compounds also rather subserves the purposes of the science, whilst that of mixtures belongs to the practical purposes of life. If, for instance, I analyze the salt of an acid, the result of the analysis will give me the constitution of that acid, its combining proportion, saturating capacity, &c.; or, in other words, the results obtained will enable me to answer a series of questions of which the solution is important for the theory of chemical science: but if, on the other hand, I analyze gunpowder, alloys, medicinal mixtures, ashes of plants, &c., &c., I have a very different object in view; I do not want in such cases to apply the results which I may obtain to the solution of any theoretical question in chemistry, but I want to render a practical service either to the arts and industries, or to some other science. If in the analysis of a chemical compound I wish to control the results obtained, I may do this in most cases by means of calculations based on stoïchiometric data, but in the case of a mixture a second analysis is necessary to confirm the correctness of the results afforded by the first.

The preceding remarks clearly show the immense importance of quantitative analysis. It may, indeed, be averred that chemistry owes to this branch its elevation to the rank of a science, since quantitative researches have led us to discover and determine the laws which govern the combinations and transpositions of the elements. Stoïchiometry is entirely based upon the results of quantitative investigations; all rational views respecting the constitution of compounds rest upon them as the only safe and solid basis.

Quantitative analysis, therefore, forms the strongest and most powerful lever for chemistry as a science, and not less so for chemistry in its applications to the practical purposes of life, to trades, arts, manufactures, and likewise in its application to other sciences. It teaches the mineralogist the true nature of minerals, and suggests to him principles and rules for their recognition and classification. It is an indispensable auxiliary to the physiologist; and agriculture has already derived much benefit from it; but far greater benefits may be predicted. We need not expatiate here upon the advantages which medicine, pharmacy, and every branch of industry derive, either directly or indirectly, from the practical application of its results. On the other hand, the benefit thus bestowed by quantitative analysis upon the various sciences, arts, &c., has been in a measure reciprocated by some of them. Thus whilst stoïchiometry owes its establishment to quantitative analysis, the stoïchiometric laws afford us the means of controlling the results of our analyses so accurately as to justify the reliance which we now generally place on them. Again, whilst quantitative analysis has advanced the progress of arts and industry, our manufacturers in return supply us with the most perfect platinum, glass, and porcelain vessels, and with articles of india-rubbber, without which it would be next to impossible to conduct our analytical operations with the minuteness and accuracy which we have now attained.

Although the aid which quantitative analysis thus derives from stoïchiometry, and the arts and manufactures, greatly facilitates its practice, and although many determinations are considerably abbrieviated by volumetric analysis, it must be admitted, notwithstanding, that the pursuit of this branch of chemistry requires considerable expenditure of time. This remark applies especially to those who are commencing the study, for they must not allow their attention to be divided upon many things at one time, otherwise the accuracy of their results will be more or less injured. I would therefore advise every one desirous of becoming an analytical chemist to arm himself with a considerable share of patience, reminding him that it is not at one bound, but gradually, and step by step, that the student may hope to attain the necessary certainty in his work, the indispensable self-reliance which can alone be founded on one's own results. However mechanical, protracted, and tedious the operations of quantitative analysis may appear to be, the attainment of accuracy will amply compensate for the time and labor bestowed upon them; whilst, on the other hand, nothing can be more disagreeable than to find, after a long and laborious process, that our results are incorrect or uncertain. Let him, therefore, who would render the study of quantitative analysis agreeable to himself, from the very outset endeavor, by strict, nay, scrupulous adherence to the conditions laid down, to attain correct results, at any sacrifice of time. I scarcely know a better and more immediate reward of labor than that which springs from the attainment of accurate results and perfectly corresponding analyses. The satisfaction enjoyed at the success of our efforts is surely in itself a sufficient motive for the necessary expenditure of time and labor, even without looking to the practical benefits which we may derive from our operations.

The following are the substances treated of in this work :—

I. METALLOIDS, OR NON-METALLIC ELEMENTS.

Oxygen, Hydrogen, Sulphur, [*Selenium,*] *Phosphorus, Chlorine, Iodine, Bromine, Fluorine, Nitrogen, Boron, Silicon, Carbon.*

II. METALS.

Potassium, Sodium, [*Lithium,*] *Barium, Strontium, Calcium, Magnesium, Aluminium, Chromium,* [*Titanium,*] *Zinc, Manganese, Nickel, Cobalt, Iron,* [*Uranium,*] *Silver, Mercury, Lead, Copper, Bismuth, Cadmium,* [*Palladium,*] *Gold, Platinum, Tin, Antimony, Arsenic,* [*Molybdenum*].

(The elements enclosed within brackets are considered in supplementary paragraphs, and more briefly than the rest.)

I have divided my subject into three parts. In the first, I treat of quantitative analysis generally; describing, 1st, the execution of analysis; and, 2d, the calculation of the results obtained. In the second, I give a detailed description of several special analytical processes. And in the third, a number of carefully selected examples, which may serve as exercises for the groundwork of the study of quantitative analysis.

The following table will afford the reader a clear and definite notion of the contents of the whole work :—

I. GENERAL PART.

A—Execution of Analysis.

1. Operations.
2. Reagents.
3. Forms and combinations in which bodies are separated from others, or in which their weight is determined.
4. Determination of bodies in simple compounds.
5. Separation of bodies.
6. Organic elementary analysis.

B—Calculation of the Results.

II. SPECIAL PART.

1. Analysis of waters.
2. Analysis of such minerals and technical products as are most frequently brought under the notice of the chemist; including methods for ascertaining their commercial value.
3. Analysis of atmospheric air.

III. EXERCISES FOR PRACTICE.

APPENDIX.

1. Analytical experiments.
2. Tables for the calculation of analytical results.

PART I.

GENERAL PART.

DIVISION I.

THE EXECUTION OF ANALYSIS.

SECTION I.

OPERATIONS.

§ 1.

Most of the operations performed in quantitative research are the same as in qualitative analysis, and have been accordingly described in my work on that branch of analytical science. With respect to such operations I shall, therefore, confine myself here to pointing out any modifications they may require to adapt them for application in the quantitative branch; but I shall, of course, give a full description of such as are resorted to exclusively in quantitative investigations. Operations forming merely part of certain specific processes will be found described in the proper place, under the head of such processes.

I. Determination of Quantity.

§ 2.

The quantity of solids is usually determined by *weight;* the quantity of gases and fluids, in many cases by *measure;* upon the care and accuracy with which these operations are performed, depends the value of all our results; I shall therefore dwell minutely upon them.

§ 3.

1. Weighing.

To enable us to determine with precision the correct weight of a substance, it is indispensable that we should possess, 1st, a good balance, and 2d, accurate weights.

a. The Balance.

Fig. 1 represents a form of balance well adapted for analytical purposes. There are several points respecting the construction and properties of a good balance, which it is absolutely necessary for every chemist to understand. The usefulness of this instrument depends upon two points: 1st, its *accuracy*, and 2d, its *sensibility* or *delicacy*.

§ 4.

The ACCURACY of a balance depends upon the following conditions:—

a. The fulcrum or the point on which the beam rests must lie above the centre of gravity of the balance.

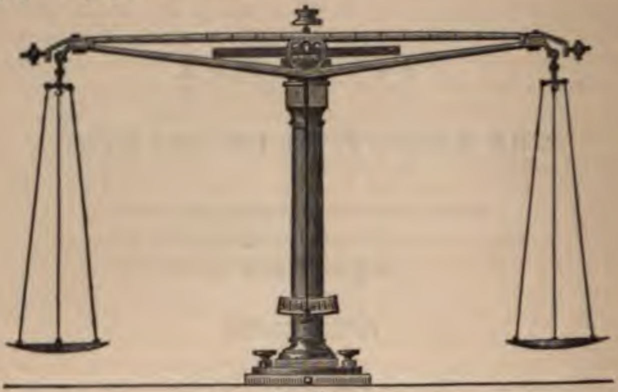

Fig. 1.

This is in fact a condition essential to every balance. If the fulcrum were placed *in* the centre of gravity of the balance, the beam would not oscillate, but remain in any position in which it is placed, assuming the scales to be equally loaded. If the fulcrum be placed *below* the centre of gravity, the balance will be overset by the slightest impulse.

When the fulcrum is above the centre of gravity the balance represents a pendulum, the length of which is equal to that of the line uniting the fulcrum with the centre of gravity, and this line forms right angles with the beam, in whatever position the latter may be placed. Now if we impart an impetus to a ball suspended by a thread, the ball, after having terminated its vibrations, will invariably rest in its original perpendicular position under the point of suspension. It is the same with a properly adjusted balance—impart an impetus to it, and it will oscillate for some time, but it will invariably return to its original position; in other words, its centre of gravity will finally fall back into its perpendicular position under the fulcrum, and the beam must consequently reassume the horizontal position.

But to judge correctly of the force with which this is accomplished, it must be borne in mind that a balance is not a simple pendulum, but a compound one, *i. e.*, a pendulum in which not one, but many material points move round the turning point. The inert mass to be moved is accordingly equal to the sum of these points, and the moving force is equal to the excess of the material points below, over those above the fulcrum.

β. The points of suspension of the scales must be on an exact level with the fulcrum. If the fulcrum be placed below the line joining the points of suspension, increased loading of the scales will continually tend to raise the centre of gravity of the whole system, so as to bring it nearer and nearer the fulcrum; the weight which presses upon the scales combining in the relatively high-placed points of suspension; at last, when the scales have been loaded to a certain degree, the centre of gravity will shift altogether to the fulcrum, and the balance will consequently cease to vibrate—any further addition of weight will finally overset the beam by placing the centre of gravity above the fulcrum. If, on the other hand, the fulcrum be placed above the line joining the points of suspension, the centre of gravity will become more and more depressed in proportion as the loading of the scales is increased; the line of the pendulum will consequently be lengthened, and a greater force will be required to produce an equal turn; in other words, the balance will grow less sensitive the greater the load. But when the three edges are in one plane, increased loading of the scales will, indeed, continually tend to raise the centre of gravity towards the fulcrum, but the former can in this case never *entirely* reach the latter, and consequently the balance will never altogether cease to vibrate upon the further addition of weight, nor will its sensibility be lessened; on the contrary—speaking theoretically—a greater degree of sensibility is imparted to it. This increase of sensibility is, however, compensated for by other circumstances. (*See* § 5.)

γ. The beam must be sufficiently rigid to bear without bending the greatest weight that the construction of the balance admits of; since the bending of the beam would of course depress the points of suspension so as to place them below the fulcrum, and this would, as we have just seen, tend to diminish the sensibility of the balance in proportion to the increase of the load. It is, therefore, necessary to avoid this fault by a proper construction of the beam. The form best adapted for beams is that of an isosceles obtuse-angled triangle, or of a rhombus.

δ. The arms of the balance must be of equal length, i.e., *the points of suspension must be equidistant from the fulcrum,* for if the arms are of unequal length the balance will not be in equilibrium, supposing the scales to be loaded with equal weights, but there will be preponderance on the side of the longer arm.

§ 5.

The SENSIBILITY of a balance depends principally upon the three following conditions:—

α. The friction of the edges upon their supports must be as slight as possible. The greater or less friction of the edges upon their supports depends upon both the form and material of those parts of the balance. The edges *must* be made of good steel, the supports *may* be made of the same material; it is better, however, that the centre edge at least should rest upon an agate plane. To form a clear conception of how necessary it is that even the end edges should have as little friction as possible, we need simply reflect upon what would happen were we to fix the scales immovably to the beam by means of rigid rods. Such a contrivance would at once altogether annihilate the sensibility of a balance, for if a weight were placed upon one scale, this certainly would have a tendency to sink; but at the same time the connecting rods being compelled to form constantly a right angle with the beam, the weighted scale would incline inwards, whilst the other scale would turn outwards, and thus the arms would become unequal, the shorter arm being on the side of the weighted scale, whereby the tendency of the latter to sink would be immediately compensated for. The more considerable the friction becomes at the end edges of a balance, the more the latter approaches the state just now described, and consequently the more is its sensibility impaired.

β. The centre of gravity must be as near as possible to the fulcrum. The nearer the centre of gravity approaches the fulcrum, the shorter becomes the pendulum. If we take two balls, the one suspended by a short and the other by a long thread, and impart the same impetus to both, the former will naturally swing at a far greater angle from its perpendicular position than the latter. The same must of course happen with a balance; the same weight will cause the scale upon which it is placed to turn the more rapidly and completely, the shorter the distance between the centre of gravity and the fulcrum. We have seen above, that in a balance where the three edges are on a level with each other, increased loading of the scales will continually tend to raise the centre of gravity towards the fulcrum. A good balance will therefore become more delicate in proportion to the increase of weights placed upon its scales; but, on the other hand, its sensibility will be diminished in about the same proportion by the increment of the mass to be moved, and by the increased friction attendant upon the increase of load; in other words, the delicacy of a good balance will remain the same, whatever may be the load placed upon it. The nearer the centre of gravity lies to the fulcrum, the slower are the oscillations of the balance. Hence in regulating the position of the centre of gravity we must not go too far, for if it approaches the fulcrum too nearly, the operation of weighing will take too much time.

γ. The beam must be as light as possible. The remarks which we have just now made will likewise show how far the weight of the beam may influence the sensibility of a balance. We have seen that if a balance is not actually to become less delicate on increased loading, it must on the one hand have a tendency to become more delicate by the continual approach of the centre of gravity to the fulcrum. Now it is evident, that the more considerable the weight of the beam is, the less will an equal load placed upon both scales alter the centre of gravity of the whole system, the more slowly will the centre of gravity approach the fulcrum, the less will the increased friction be neutralized, and consequently the less sensibility will the balance possess. Another point to be taken into account here is, that the moving forces being equal, a lesser mass or weight is more readily moved than a greater. (§ 4 α).

§ 6.

We will now proceed, first, to give the student a few general rules to guide him in the purchase of a balance intended for the purposes of quantitative analysis; and, secondly, to point out the best method of testing the accuracy and sensibility of a balance.

1. A balance able to bear 70 or 80 grammes in each scale, suffices for most purposes.

2. The balance must be enclosed in a glass case to protect it from dust. This case ought to be sufficiently large, and, more especially, its sides should not approach too near the scales. It must be constructed in a manner to admit of its being opened and closed with facility, and thus to allow the operation of weighing to be effected without any disturbing influence from currents of air. Therefore, either the front part of the case should consist of three parts, viz., a fixed centre part and two lateral parts, opening like doors; or, if the front part happens to be made of one piece, and arranged as a sliding-door, the two sides of the case must be provided each with a door.

3. The balance must be provided with a proper contrivance to render it immovable whilst the weights are being placed upon the scale. This is most commonly effected by an arrangement which enables the operator to lift up the beam and thus to remove the middle edge from its support, whilst the scales remain suspended.

It is highly advisable to have the case of the balance so arranged that the contrivances for lifting the beam and fixing the scales can be worked while the case remains closed, and consequently from without.

4. It is necessary that the balance should be provided with an index to mark its oscillations; this index is appropriately placed at the bottom of the balance.

5. The balance must be provided with a spirit level, to enable the operator to place the three edges on an exactly horizontal level; it is best also for this purpose that the case should rest upon three screws.

6. It is very desirable that the beam should be graduated into tenths, so as to enable the operator to weigh the milligramme and its fractions with a centigramme "rider." *

7. The balance must be provided with a screw to regulate the centre of gravity, and likewise with two screws to regulate the equality of the arms, and finally with screws to restore the equilibrium of the scales, should this have been disturbed.

§ 7.

The following experiments serve to test the accuracy and sensibility of a balance.

1. The balance is, in the first place, accurately adjusted, if necessary, either by the regulating screws, or by means of tinfoil, and a milligramme weight is then placed in one of the scales. A good and practically useful balance must turn very distinctly with this weight; a delicate chemical balance should indicate the $\frac{1}{10}$ of a milligramme with perfect distinctness.

2. Both scales are loaded with the maximum weight the construction of the balance will admit of—the balance is then *accurately* adjusted, and a milligramme added to the weight in the one scale. This ought to cause the balance to turn to the same extent as in 1. In most balances, however, it shows somewhat less on the index. It follows from § 5 β that the balance will oscillate more slowly in this than in the first experiment.

3. The balance is accurately adjusted, (should it be necessary to establish a perfect equilibrium between the scales by loading the one with a minute portion of tinfoil, this tinfoil must be left remaining upon the scale during the experiment); both scales are then equally loaded, say, with fifty grammes each, and, if necessary, the balance is again adjusted (by the addition of small weights). The load of the two scales is then interchanged, so as to transfer that of the right scale to the left, and *vice versâ*. A balance with perfectly equal arms must maintain its absolute equilibrium upon this interchange of the weights of the two scales.

4. The balance is accurately adjusted; it is then arrested and again set in motion; the same process should be repeated several times. A good balance must invariably reassume its original equilibrium. A balance the end edges of which afford too much play to the hook resting upon

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* [Becker's later balances have beams graduated to twelfths, and a rider weighing 12 mgrs. This enables the operator to use nearly the whole of the graduation.]

them, so as to allow the latter slightly to alter its position, will show perceptible differences in different trials. This fault, however, is possible only with balances of defective construction.

A balance to be practically useful for the purposes of quantitative analysis *must* stand the first, second, and last of these tests. A slight inequality of the arms is of no great consequence, as the error that it would occasion may be completely prevented by the manner of weighing.

As the sensibility of a balance will speedily decrease if the steel edges are allowed to get rusty, delicate balances should never be kept in the laboratory, but always in a separate room. It is also advisable to place within the case of the balance a vessel half filled with calcined carbonate of potassa, to keep the air dry. I need hardly add that this salt must be re-calcined as soon as it gets moist.

§ 8.

b. The Weights.

1. The French gramme is the best standard for calculation. A set of weights ranging from fifty grammes to one milligramme may be considered sufficient for all practical purposes. With regard to the set of weights, it is generally a matter of indifference for scientific purposes whether the gramme, its multiples and fractions, are really and perfectly equal to the accurately adjusted *normal* weights of the corresponding denominations;* but it is *absolutely necessary* that they should agree *perfectly* with each other, *i.e.*, the centigramme weight must be exactly the one hundredth part of the gramme weight of the set, &c. &c.

2. The whole of the set of weights should be kept in a suitable, well-closing box; and it is desirable likewise that a distinct compartment be appropriated to every one even of the smaller weights.

3. As to the shape best adapted for weights, I think that of short frusta of cones inverted, with a handle at the top, the most convenient and practical form for the large weights; square pieces of foil, turned up at one corner, are best adapted for the small weights. The foil used for this purpose should not be too thin, and the compartments adapted for the reception of the several smaller weights in the box, should be large enough to admit of their contents being taken out of them with facility, or else the smaller weights will soon get cracked, bruised, and indistinct. Every one of the weights (with the exception of the milligramme) should be distinctly marked.

4. With respect to the material most suitable for the manufacture of weights, we commonly rest satisfied with having the smaller weights only, from 1 or 0·5 gramme downwards, made of platinum or aluminium foil, using brass weights for all the higher denominations. Brass weights must be carefully shielded from the contact of acid or other vapors, or their correctness will be impaired; nor should they ever be touched with the fingers, but always with small pincers. But it is an erroneous notion to suppose that weights slightly tarnished are unfit for use. It is,

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* Still it would be desirable that mechanicians who make gramme-weights intended for the use of the chemist, should endeavor to procure *normal* weights. It is very inconvenient, in many cases, to find notable differences between weights of the same denomination, but coming from different makers; as I myself have often had occasion to discover.

indeed, hardly possible to prevent weights for any very great length of time from getting slightly tarnished. I have carefully examined many weights of this description, and have found them as exactly corresponding with one another in their relative proportions as they were when first used. The tarnishing coat, or incrustation, is so extremely thin, that even a very delicate balance will generally fail to point out any perceptible difference in the weight.

The following is the proper way of *testing the weights*:—

One scale of a delicate balance is loaded with a one-gramme weight, and the balance is then completely equipoised by taring with small pieces of brass, and finally tinfoil (not paper, since this absorbs moisture). The weight is then removed, and replaced successively by the other gramme weights, and afterwards by the same amount of weight in pieces of lower denominations.

The balance is carefully scrutinized each time, and any deviation from the exact equilibrium marked. In the same way it is seen whether the two-gramme piece weighs the same as two single grammes, the five-gramme piece the same as three single grammes and the two-gramme piece, &c. In the comparison of the smaller weights thus among themselves, they must not show the least difference on a balance turning with $\frac{1}{10}$ of a milligramme. In comparing the larger weights with all the small ones, differences of $\frac{1}{10}$ to $\frac{2}{10}$ of a milligramme may be passed over. If you wish them to be more accurate, you must adjust them yourself. In the purchase of weights chemists ought always to bear in mind that an accurate weight is truly valuable, whilst an inaccurate one is absolutely worthless. It is the safest way for the chemist to test every weight he purchases, no matter how high the reputation of the maker.

§ 9.

c. THE PROCESS OF WEIGHING.

We have two different methods of determining the weight of substances; the one might be termed *direct weighing*, the other is called *weighing by substitution*.

In *direct weighing*, the substance is placed upon one scale, and the weight upon the other. If we possess a balance, the arms of which are of equal length, and the scales in a perfect state of equilibrium, it is indifferent upon which scale the substance is placed in the several weighings required during an analytical process; *i.e.*, we may weigh upon the right or upon the left side, and change sides at pleasure, without endangering the accuracy of our results. But if, on the contrary, the arms of our balance are not perfectly equal, or if the scales are not in a state of perfect equilibrium, we are compelled to weigh invariably upon the same scale, otherwise the correctness of our results will be more or less materially impaired.

Suppose we want to weigh one gramme of a substance, and to divide this amount subsequently into two equal parts. Let us assume our balance to be in a state of perfect equilibrium, but with unequal arms, the left being 99 millimetres, the right 100 millimetres long; we place a gramme weight upon the left scale, and against this, on the right scale, as much of the substance to be weighed as will restore the equilibrium of the balance.

According to the axiom, "masses are in equilibrium upon a lever, if the products of their weights into their distances from the fulcrum are equal," we have consequently upon the right scale 0·99 grm. of substance, since 99 × 1·00=100 × 0·99. If we now, for the purpose of weighing one half the quantity, remove the whole weight from the left scale, substituting a 0·5 grm. weight for it, and then take off part of the substance from the right scale, until the balance recovers its equilibrium, there will remain 0·495 grm.; and this is exactly the amount we have removed from the scale: we have consequently accomplished our object with respect to the relative weight; and, as we have already remarked, the absolute weight is not generally of so much importance in scientific work. But if we attempted to halve the substance which we have on the right scale, by first removing both the weight and the substance from the scales, and placing subsequently a 0·5 grm. weight upon the *right* scale, and part of the substance upon the *left*, until the balance recovers its equilibrium, we should have 0·505 of substance upon the left scale, since 100 × 0·500=99 × 0·505; and consequently, instead of exact halves, we should have one part of the substance amounting to 0·505, the other only to 0·485.

If the scales of our balance are not in a state of absolute equilibrium, we are obliged to weigh our substances in vessels to insure accurate results (although the arms of the balance be perfectly equal). It is self-evident that the weights in this case must likewise be invariably placed upon one and the same scale, and that the difference between the two scales must not undergo the slightest variation during the whole course of a series of experiments.

From these remarks result the two following rules:—

1. It is, under all circumstances, advisable to place the substance invariably upon one and the same scale—most conveniently upon the left.
2. If the operator happens to possess a balance for his own private and *exclusive* use, there is no need that he should adjust it at the commencement of every analysis; but if the balance be used in common by several persons, it is absolutely necessary to ascertain, before every operation, whether the state of absolute equilibrium may not have been disturbed.

Weighing by substitution yields not only *relatively*, but also *absolutely* accurate results; no matter whether the arms of the balance be of exactly equal lengths or not, or whether the scales be in perfect equipoise or not.

The process is conducted as follows: the material to be weighed—say a platinum crucible—is placed upon one scale, and the other scale is accurately counterpoised against it. The platinum crucible is then removed, and the equilibrium of the balance restored by substituting weights for the removed crucible. It is perfectly obvious that the substituted weights will invariably express the real weight of the crucible with absolute accuracy. We weigh by substitution whenever we require the greatest possible accuracy; as, for instance, in the determination of atomic weights. The process may be materially shortened by first placing a tare (which must of course be heavier than the substance to be weighed) upon one scale, say the left, and loading the other scale with weights until equilibrium is produced. This tare is always retained on the left scale. The weights after being noted are removed. The substance is placed on the right scale, together with the smaller weights requisite to restore the equilibrium of the balance. The sum of the weights added is then subtracted from the noted weight of the counterpoise: the remainder will at once indicate the absolute weight of the substance. Let us suppose, for instance, we have on the left scale a tare requiring a weight of fifty grammes to counterpoise it. We place a platinum crucible on the right scale, and find that it requires an addition of weight to the extent of 10 grammes to counterpoise the tare on the left. Accordingly, the crucible weighs 50 minus 10=40 grammes.

§ 10.

The following *rules* will be found useful in performing the process of weighing:—

1. The safest and most expeditious way of ascertaining the exact weight of a substance, is to avoid trying weights at random; instead of this, a strictly systematic course ought to be pursued in counterpoising substances on the balance. Suppose, for instance, we want to weigh a crucible, the weight of which subsequently turns out to be 6·627 grammes; well, we place 10 grammes on the other scale against it, and we find this is too much; we place the weight next in succession, *i.e.*, 5 grammes, and find this too little; next 7, too much; 6, too little; 6·5, too little; 6·7, too much; 6·6, too little; 6·65, too much; 6·62, too little; 6·63, too much; 6·625, too little; 6·627, right.

I have selected here, for the sake of illustration, a most complicated case; but this systematic way of laying on the weights will in most instances lead to the desired end, in half the time required when weights are tried at random. After a little practice a few minutes will suffice to ascertain the weight of a substance to within the $\frac{1}{10}$ of a milligramme, provided the balance does not oscillate too slowly.

2. The milligrammes and fractions of milligrammes are determined by a centigramme rider (to be placed on or between the divisions on the beam) far more expeditiously and conveniently than by the use of the weights themselves, and at the same time with equal accuracy.

3. Particular care and attention should be bestowed on entering the weights in the book. The best way is to write down the weights first by inference from the blanks, or gaps in the weight box, and to control the entry subsequently by removing the weights from the scale, and replacing them in their respective compartments in the box. The student should from the commencement make it a rule to enter the number to be deducted in the *lower line*; thus, in the upper line, the weight of the crucible + the substance; in the lower line, the weight of the empty crucible.

4. The balance ought to be arrested every time any change is contemplated, such as removing weights, substituting one weight for another, &c. &c., or it will soon get spoiled.

5. Substances (except, perhaps, pieces of metal, or some other bodies of the kind) must never be placed *directly* upon the scales, but ought to be weighed in appropriate vessels of platinum, silver, glass, porcelain, &c., never on paper or card, since these, being liable to attract moisture, are apt to alter in weight. The most common method is to weigh in the first instance the vessel by itself, and to introduce subsequently the substance into it; to weigh again, and subtract the former weight from the latter. In many instances, and more especially where several portions of the same substance are to be weighed, the united weight of the vessel and of its contents is first ascertained; a portion of the contents is then shaken out, and the vessel weighed again; the loss of weight expresses the amount of the portion taken out of the vessel.

6. Substances liable to attract moisture from the air, must be weighed invariably in closed vessels (in covered crucibles, for instance, or between two watch-glasses, or in a closed glass tube); fluids are to be weighed in small bottles closed with glass stoppers.

7. A vessel ought never to be weighed whilst warm, since it will in that case invariably weigh lighter than it really is. This is owing to two circumstances. In the first place, every body condenses upon its surface a certain amount of air and moisture, the quantity of which depends upon the temperature and hygroscopic state of the air, and likewise on its own temperature. Now suppose a crucible has been weighed cold at the commencement of the operation, and is subsequently weighed again whilst hot, together with the substance it contains, and the weight of which we wish to determine. If we subtract for this purpose the weight of the cold crucible, ascertained in the former instance, from the weight found in the latter, we shall subtract too much, and consequently we shall set down less than the real weight for the substance. In the second place, bodies at a high temperature are constantly communicating heat to the air immediately around them; the heated air expands and ascends, and the denser and colder air, flowing towards the space which the former leaves, produces a current which tends to raise the scale, making it thus appear lighter than it really is.

8. If we suspend from the end edges of a correct balance respectively 10 grammes of platinum and 10 grammes of glass, by wires of equal weight, the balance will assume a state of equilibrium; but if we subsequently immerse the platinum and glass completely in water, this equilibrium will at once cease, owing to the different specific gravity of the two substances; since, as is well known, substances immersed in water lose of their weight a quantity equal to the weight of their own bulk of water. If this be borne in mind, it must be obvious to every one that weighing in the air is likewise defective, inasmuch as the bulk of the substance weighed is not the same with that of the weight. This defect, however, is so very insignificant, owing to the trifling specific gravity of the air in proportion to that of solid substances, that we may generally disregard it altogether in analytical experiments. In cases, however, where *absolutely* accurate results are required, the bulk both of the substance examined, and of the weight, must be taken into account, and the weight of the corresponding volume of air added respectively to that of the substance and of the weight, making thus the process equivalent to weighing *in vacuo.*

§ 11.

2. MEASURING.

The process of measuring is confined in analytical researches mostly to gases and liquids. The method of measuring gases has been brought to such perfection that it may be said to equal in accuracy the method of weighing. However, such accurate measurements demand an expenditure of time and care, which can be bestowed only on the nicest and most delicate scientific investigations.*

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* [The student who will practise the accurate measurement of gases in any but the simplest cases, must refer for all details to Bunsen's "Gasometry" (translated by Roscoe), and Russell, Jour. Chem. Soc., 1868 p.128, as the subject is too extensive for the limits of this volume.]

The measuring of liquids in analytical investigations was resorted to first by DESCROIZILLES ("Alkalimeter," 1806). GAY-LUSSAC materially improved the process, and indeed brought it to the highest degree of perfection (measuring of the solution of chloride of sodium in the assay of silver in the wet way). More recently F. MOHR* has bestowed much care and ingenuity upon the production of appropriate and convenient measuring apparatus, and has added to our store the eminently practical *compression stop-cock burette.* The process is now resorted to even in most accurate scientific investigations, since it requires much less time than the process of weighing.

The accuracy of all measurings depends upon the proper construction of the measuring vessels, and also upon the manner in which the process is conducted.

§ 12.

a. THE MEASURING OF GASES.

We use for the measuring of gases graduated tubes of greater or less capacity, made of strong glass, and closed by fusion at one end, which should be rounded. The following tubes will be found sufficient for all the processes of gas measuring required in organic elementary analyses.

1. A bell-glass capable of holding from 150 to 250 c. c., and about 4 centimetres in diameter; divided into cubic centimetres.

2. Five or six glass tubes, about 12 to 15 millimetres in diameter in the clear, and capable of holding from 30 to 40 c. c. each, divided into $\frac{1}{5}$ c. c.

The sides of these tubes should be pretty thick, otherwise they will be liable to break, especially when used to measure over mercury. The sides of the bell-glass should be about 3, of the tubes about 2 millimetres thick.

The most important point, however, in connection with measuring instruments is that they be correctly graduated, since upon this of course depends the accuracy of the results. For the method of graduating I refer to GREVILLE WILLIAMS' "Chemical Manipulation." †

In testing the measuring tubes we have to consider three things.

1. Do the divisions of a tube correspond with each other?

2. Do the divisions of each tube correspond with those of the other tubes?

3. Do the volumes expressed by the graduation lines correspond with the weights used by the analyst?

These three questions are answered by the following experiments:

a. The tube which it is intended to examine is placed in a perpendicular position, and filled gradually with accurately measured small quantities of mercury, care being taken to ascertain with the utmost precision whether the graduation of the tube is proportionate to the equal volumes of mercury poured in. The measuring-off of the mercury is effected by means of a small glass tube, sealed at one end, and ground perfectly even and smooth at the other. This tube is filled to overflowing by immersion under mercury, care being taken to allow no air bubbles to remain in it; the excess of mercury is then removed by pressing a small glass plate down on the smooth edge of the tube.*

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* "Lehrbuch der Titrirmethode," by Dr. Fr. Mohr. Brunswick, 1855.

† [See also Cary Lea, Am. Jour. Sci. and Arts, 2d ser., vol. 42, p. 375.]

b. Different quantities of mercury are successively measured off in one of the smaller tubes, and then transferred into the other tubes. The tubes may be considered in perfect accordance with each other, if the mercury reaches invariably the same divisional point in every one of them.

Such tubes as are intended simply to determine the relative volume of different gases, need only pass these two experiments; but in cases where we want to calculate the *weight* of a gas from its *volume*, it is necessary also to obtain an answer to the third question. For this purpose—

c. One of the tubes is accurately weighed and then filled with distilled water of a temperature of 16° to the last mark of the graduated scale; the weight of the water is then accurately determined. If the tube agrees with the weights, every 100 c. c. of water of 16° must weigh 99·9 grm. But should it not agree, no matter whether the error lie in the graduation of the tube or in the adjustment of the weights, we must apply a correction to the volume observed before calculating the weight of a gas therefrom. Let us suppose, for instance, that we find 100 c. c. to weigh only 99·6 grm.: assuming our weights to be correct, the c. c. of our scale are accordingly too small; and to convert 100 of these c. c. into normal c. c. we say:—

$$99{\cdot}9 : 99{\cdot}6 :: 100 : x.$$

In the measuring of gases we must have regard to the following points:—

1. Correct reading-off. 2. The temperature of the gas. 3. The degree of pressure operating upon it. And 4. The circumstance whether it is dry or moist. The three latter points will be readily understood, if it be borne in mind that any alteration in the temperature of a gas, or in the pressure acting upon it, or in the tension of the admixed aqueous vapor, involves likewise a considerable alteration in its volume.

§ 13.

1. Correct Reading-off.

This is rather difficult, since mercury in a cylinder has a convex surface (especially observable with a narrow tube), owing to its own cohesion; whilst water, on the other hand, under the same circumstances has a concave surface, owing to the attraction which the walls of the tube exercise upon it. The cylinder should invariably be placed in a perfectly perpendicular position, and the eye of the operator brought to a level with the surface of the fluid.

In reading-off over water, the middle of the dark zone formed by that portion of the liquid that is drawn up around the inner walls of the tube, is assumed to be the real surface; whilst when operating with mercury, we have to place the real surface in a plane exactly in the middle between the highest point of the surface of the mercury, and the points at which the latter is in actual contact with the walls of the tube. However, the results obtained in this way are only approximate.

Absolutely accurate results cannot be arrived at, in measuring over water or any other fluid that adheres to glass. But over mercury they may be arrived at if the error of the meniscus be determined and the mercury be read off at the highest point. The determination of the error of the meniscus is performed for each tube, once for all, in the following manner: some mercury is poured into the tube, and its height read-off right on a level with the top of the convex surface exhibited by it; a few drops of solution of chloride of mercury are then poured on the top of the metal; this causes the convexity to disappear; the height of the mercury in the tube is now read-off again and the difference noted. In the process of graduation, the tube stands upright, in that of measuring gases, it is placed upside down; the difference observed must accordingly be doubled, and the sum added to each volume of gas read off.

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* As warming the metal is to be carefully avoided in this process, it is advisable not to hold the tube with the hand in immersing it in the mercury, but to fasten it in a small wooden holder.

§ 14.

2. INFLUENCE OF TEMPERATURE.

The temperature of gases to be measured is determined either by making it correspond with that of the confining fluid, and ascertaining the latter, or by suspending a delicate thermometer by the side of the gas to be measured, and noting the degree which it indicates.

If the construction of the pneumatic apparatus permits the total immersion of the cylinder in the confining fluid, uniformity of temperature between the latter and the gas which it is intended to measure, is most readily and speedily obtained; but in the reverse case, the operator must always, after every manipulation, allow half an hour or, in operations combined with much heating, even an entire hour to elapse, before proceeding to observe the state of the mercury in the cylinder, and in the thermometer.

Proper care must also be taken, after the temperature of the gas has been duly adjusted, to prevent re-expansion during the reading-off; all injurious influences in this respect must accordingly be carefully guarded against, and the operator should, more especially, avoid laying hold of the tube with his hand (in pressing it down, for instance, into the confining fluid); making use, instead, of a wooden holder.

§ 15.

3. INFLUENCE OF PRESSURE.

With regard to the third point, the gas is under the actual pressure of the atmosphere if the confining fluid stands on an exact level both in and outside the cylinder; the degree of pressure exerted upon it may therefore at once be ascertained by consulting the barometer. But if the confining fluid stands *higher* in the cylinder than outside, the gas is under *less* pressure,—if *lower*, it is under *greater* pressure than that of the atmosphere; in the latter case, the perfect level of the fluid inside and outside the cylinder may readily be restored by raising the tube; if the fluid stands higher in the cylinder than outside, the level may be restored by depressing the tube; this however can only be done in cases where we have a trough of sufficient depth. When operating over water, the level may in most cases be readily adjusted; when operating over mercury, it is, more especially with wide tubes, often impossible to bring the fluid to a perfect level inside and outside the cylinder.

§ 16.

4. INFLUENCE OF MOISTURE.

In measuring gases saturated with aqueous vapor, it must be taken into account that the vapor, by virtue of its tension, exerts a pressure upon the confining fluid. The necessary correction is simple, since we know the respective tension of aqueous vapor for the various degrees of temperature. But before this correction can be applied, it is, of course, necessary that the gas should be actually saturated with the vapor. It is, therefore, indispensable in measuring gases to take care to have the gas thoroughly saturated with aqueous vapor, or else absolutely dry.

It is quite obvious from the preceding remarks, that volumes of gases can be compared only if measured at the same temperature, under the same pressure, and in the same hygroscopic state. They are generally reduced to 0°, 0·76 met. barometer, and absolute dryness. How this is effected, as well as the manner in which we deduce the weight of gases from their volume, will be found in the chapter on the calculation of analyses.

§ 17.

B. THE MEASURING OF FLUIDS.

In consequence of the vast development which volumetric analysis has of late acquired, the measuring of fluids has become an operation of very frequent occurrence. According to the different objects in view, various kinds of measuring vessels are employed. The operator must, in the case of every measuring vessel, carefully distinguish whether it is graduated for *holding* or for *delivering* the exact number of c. c. marked on it. If you have made use of a vessel of the former description in measuring off 100 c. c. of a fluid, and wish to transfer the latter completely to another vessel, you must, after emptying your measuring vessel, rinse it, and add the rinsings to the fluid transferred; whereas, if you have made use of a measuring vessel of the latter description, there must be no rinsing.

a. MEASURING VESSELS GRADUATED FOR HOLDING THE EXACT MEASURE OF FLUID MARKED ON THEM.

aa. Measuring vessels which serve to measure out one definite quantity of fluid.

We use for this purpose—

§ 18.

1. *Measuring Flasks.*

Fig. 2 represents a measuring flask of the most practical and convenient form.

Measuring flasks of various sizes are sold in the shops, holding respectively [illegible], &c., c. c. As a general rule, they have no ground-glass stoppers; it is, however, very desirable, in certain cases, to have measuring flasks with ground stoppers. The flasks must be made of well-annealed glass of uniform thickness, so that fluids may be heated in them. The line-mark should be placed within the lower third, or at least within the lower half, of the neck.

Measuring flasks, before they can properly be employed in analytical operations, must first be carefully tested. The best and simplest way of effecting this is to proceed thus:—Put the flask, perfectly dry inside and outside, on the one scale of a sufficiently delicate balance, together with a weight of 1000 grm. in the case of a litre flask, 500 grm. in the case of a half-litre flask, &c., restore the equilibrium by placing the requisite quantity of shot and tinfoil on the other scale, then remove the flask and the weight from the balance, put the flask on a perfectly level surface, and pour in distilled water of 16°,* until the lower border of the dark zone formed by the top of the water around the inner walls corresponds with the line-mark. After having thoroughly dried the neck of the flask above the mark, replace it upon the scale: if this restores the perfect equilibrium of the balance, the water in the flask weighs, in the case of a litre-measure, exactly 1000 grm. If the scale bearing the flask sinks, the water in it weighs as much above 1000 grm. as the additional weights amount to which you have to put in the other scale to restore the equilibrium; if it rises, on the other hand, the water weighs as much less as the weights amount to which you have to put in the scale with the flask to effect the same end.

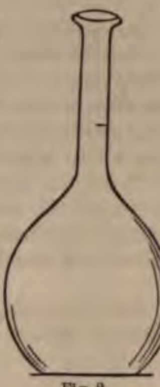

Fig. 2.

If the water in the litre-measure weighs 999 grm.,† in the half-litre measure, 499·5 grm., &c., the measuring flasks are correct. Differences up to 0·100 grm., in the litre measure, up to 0·070 grm. in the half-litre measure, and up to 0·050 grm. in the quarter-litre measure, are not taken into account, as one and the same measuring-flask will be found to offer variation to the extent indicated, in repeated consecutive weighings, though filled each time exactly up to the mark with water of the same temperature.

Though a flask should, upon examination, turn out not to hold the exact quantity of water which it is stated to contain, it may yet possibly agree with the other measuring vessels, and may accordingly still be perfectly fit for use for most purposes. Two measuring vessels agree among themselves if the marked Nos. of c. c. bear the same proportion to each other as the weights found; thus, for instance, supposing your litre-measure to hold 998 grm. water of 16°, and your 50 c. c. pipette to deliver 49·9 grm. water of the same temperature, the two measures agree, since

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* To use water in the state of its highest density, viz., of 4°, 1 c. c. of which weighs exactly 1 grm., and, accordingly, 1 litre, exactly 1000 grms., is less practical, as the operations must in that case be conducted in a room as cold; since, in a warmer room, the outside of the flask would immediately become covered with moisture, in consequence of the air cooling below dew-point. Nor can I recommend F. Mohr's suggestion to make litre-flasks, and measuring vessels in general, upon a plan to make the litre-flask, for instance, hold, not 1000 grm. water at 4°, but 1000 grm. at 16°, since in an arrangement of the kind proper regard is not paid to the actual meaning of the term "litre" in the scientific world; and measuring-vessels of the same nominal capacity, made by different instrument-makers, are thus liable to differ to a greater or less extent. One litre-flask, according to Mohr, holds 1001·2 standard c. c. I consider it impractical to give to the c. c. another signification in vessels intended for measuring fluids than in vessels used for the measuring of gases, which latter demand strict adhesion to the standard c. c., as it is often required to deduce the weight of a gas by calculating from the volume.

† With absolute accuracy, 998·981 grm.

$$1000 : 50 = 998 : 49·9.$$

To prepare or correct a measuring flask, tare the dry litre, half litre, or quarter-litre flask, and then weigh into it, by substitution (§ 9) 999 grm., or, as the case may be, the half or quarter of that quantity of distilled water of 16°. Put the flask on a perfectly horizontal support, place your eye on an exact level with the surface of the water, and mark the lower border of the dark zone by two little dots made on the glass with a point dipped into thick asphaltum varnish, or some other substance of the kind. Now pour out the water, place the flask in a convenient position, and cut with a diamond a fine distinct line into the glass from one dot to the other.

bb. Measuring vessels which serve to measure out any quantities of fluid at will.

§ 19.

2. *The Graduated Cylinder.*

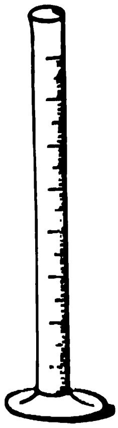

Fig. 3.

This instrument, represented in fig. 3, should be from 2 to 3 cm. wide, of acapacity of 100—300 c. c., and divided into single c. c. It must be ground at the top, that it may be covered quite close with a ground-glass plate. The measuring with such cylinders is not quite so accurate as with measuring flasks, as in the latter the volume is read off in a narrower part. The accuracy of measuring cylinders may be tested in the same way as in the case of measuring flasks, viz., by weighing into them water of 16°; or, also, very well, by letting definite quantities of fluid flow into the cylinder from a correct pipette, or burette graduated for delivering, and observing whether or not they are correctly indicated by the scale of the cylinder.

β. MEASURING VESSELS GRADUATED FOR DELIVERING THE EXACT MEASURE OF FLUID MARKED ON THEM (graduated *à l'écoulement*).

aa. Measuring vessels which serve to measure out one definite quantity of fluid.

§ 20.

3. *The Graduated Pipette.*

This instrument serves to take out a definite volume of a fluid from one vessel, and to transfer it to another; it must accordingly be of a suitable shape to admit of its being freely inserted into flasks and bottles.

We use pipettes of 1, 5, 10, 20, 50, 100, 150, and 200 c. c. capacity. The proper shape for pipettes up to 20 c. c. capacity is represented in fig. 4; fig. 5 shows the most practical form for larger ones. To fill a pipette suction is applied to the upper aperture, either directly with the lips or through a caoutchouc-tube, until the fluid stands above the mark; the upper orifice (which is somewhat narrowed and ground) is then closed with the first finger of the right hand (the point of which should be a little moist); the outside is then wiped dry, if required, and, the pipette being held in a perfectly vertical direction, the fluid is made to drop out, by lifting the finger a little, till it has fallen to the required level; the loose drop is carefully wiped off, and the contents of the tube are then finally transferred to the other vessel. In this process it is found that the fluid does not run out completely, but that a small portion of it remains adhering to the glass in the point of the pipette; after a time, as this becomes increased by other minute particles of fluid trickling down from the upper part of the tube, a drop gathers at the lower orifice, which may be allowed to fall off from its own weight, or may be made to drop off by a slight shake. If, after this, the point of the pipette be laid against a moist portion of the inner side of the vessel, another minute portion of fluid will trickle out, and, lastly, another trifling droplet or so may be got out by blowing into the pipette. Now, supposing the operator follows no fixed rule in this respect, letting the fluid, for instance, in one operation simply run out, whilst in another operation he lets it drain afterwards, and in a third blows out the last particles of it from the pipette, it is evident that the respective quantities of fluid delivered in the several operations cannot be quite equal. I prefer in all cases the second method, viz., to lay the point of the pipette, whilst draining, finally against a moist portion of the side of the vessel, which I have always found to give the most accurately corresponding measurements.

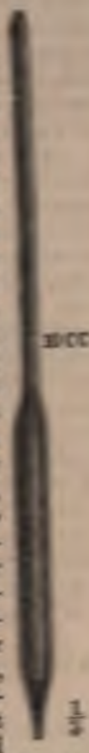

Fig. 4.

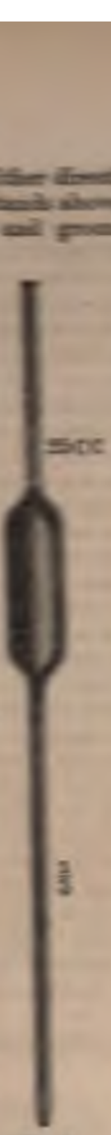

Fig. 5.

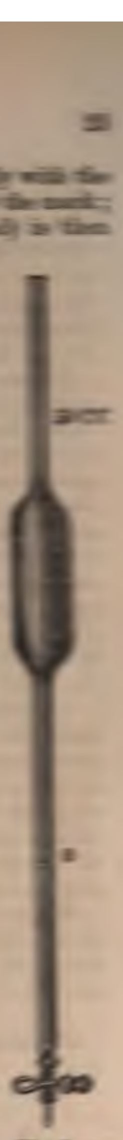

Fig. 6.

The correctness of a pipette is tested by filling it up to the mark with distilled water of 16°, letting the water run out, in the manner just stated, into a tared vessel, and weighing; the pipette may be pronounced correct if 100 c. c. of water of 16° weigh 99·9 grm.

Testing in like manner the accuracy of the measurements made with a simple hand pipette, we find that one and the same pipette will in repeated consecutive weighings of the contents, though filled and emptied each time with the minutest care, show differences up to 0·010 grm. for 10 c. c. capacity, up to 0·040 grm. for 50 c. c. capacity.

The accuracy of the measurements made with a pipette may be heightened by giving the instrument the form and construction shown in fig. 6, and fixing it to a holder.

It will be seen from the drawing that these pipettes are emptied only to a certain mark in the lower tube, and that they are provided with a *compression stop-cock*, a contrivance which we shall have occasion to describe in detail when on the subject of burettes. This contrivance reduces the differences of measurements with one and the same 50 c. c. pipette to 0·005 grm.

Pipettes are used more especially in cases where it is intended to estimate different constituents of a substance in separate portions of the same: for instance, 10 grm. of the substance under examination are dissolved in a 250 c. c. flask, the solution is diluted up to the mark, shaken, and 2, 3, or 4 several portions are then taken out with a 50 c. c. pipette. Each portion consists of ⅕ part of the whole, and accordingly contains 2 grm. of the substance. Of course the pipette and the flask must be in perfect harmony. Whether they are may be ascertained by, for instance, emptying the 50 c. c. pipette 5 times into the 250 c. c. flask, and observing if the lower edge of the dark zone of fluid coincides with the mark. If it does not, you may make a fresh mark, which, no matter whether it is really correct or not, will bring the two instruments in question into conformity with each other.

Cylindrical pipettes, graduated throughout their entire length, may be used also to measure out any given quantities of liquid; however, these instruments can properly be employed only in processes where minute accuracy is not indispensable, as the limits of error in reading off the divisions in the wider part of the tube are not inconsiderable. For smaller quantities of liquid this inaccuracy may be avoided, by making the pipettes of tubes of uniform width, having a small diameter only, and narrowed at both ends. (Fr. Mohr's measuring pipettes.)

When a fluid runs out of a pipette, drops sometimes remain here and there adhering to the tube; this arises from a film of fat on the inside; it may be removed by keeping the instrument some time filled with a solution of bichromate of potassa mixed with sulphuric acid.

bb. Measuring vessels which serve to measure out quantities of fluid at will.

4. *The Burette.*

Of the various forms and dispositions of this instrument, the following appear to me the most convenient:—

§ 21.

1. *Mohr's Burette.* (Compression cock burette.)

For this excellent measuring apparatus, which is represented in fig. 7, we are indebted to Fr. Mohr. It consists of a cylindrical tube, narrowed towards the lower end for about an inch, with a slight widening, however, at the extreme point, in order that the caoutchouc connector may take a firm hold. I only use burettes of two sizes, viz., of 30 c. c., divided into $\frac{1}{10}$ c. c., and of 50 c. c. divided into ⅕ c. c. The former I employ principally in scientific, the latter chiefly in technical investigations. The usual length of my 30 c. c. burette is about 50 cm.; the graduated portion occupies about 49 cm. The diameter of the tube is accordingly about 10 mm. in the clear; the upper orifice is, for the convenience of filling, widened in form of a funnel, measuring 20 mm. in diameter; the width of the lower orifice is 5 mm. For very delicate processes, the length of the graduated portion may be extended to 50 or 52 cm., leaving thus intervals of nearly 2 mm. between the small divisional lines. In my 50 c. c. burettes the graduated portion of the tube is generally 40 cm. long.

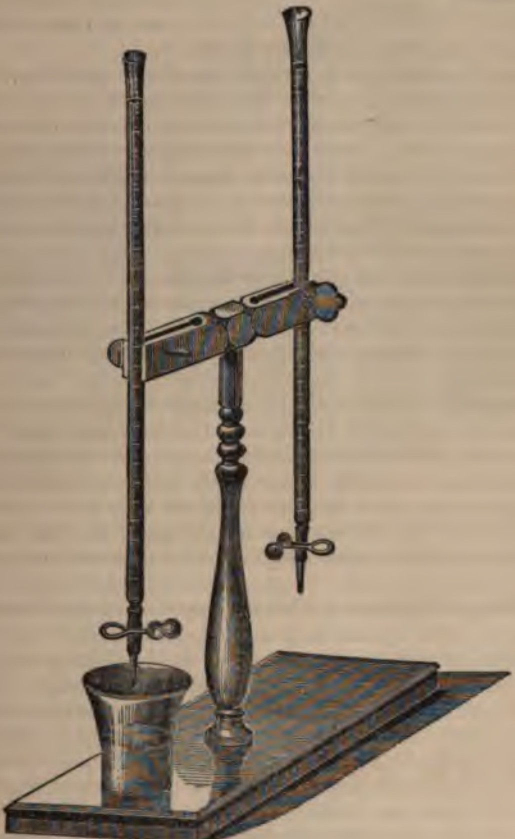

Fig. 7.

To make the instrument ready for use, the narrowed lower end of the tube is warmed a little, and greased with tallow; a caoutchouc tube, about 30 mm. long, and having a diameter of 3 mm. in the clear, is then drawn over it; into the other end of this is inserted a tube of pretty thick glass, about 40 mm. long, and drawn out to a tolerably fine point; it is advisable to slightly widen the upper end of this tube also, and to cover it with a thin coat of tallow; and also to tie linen-thread, or twine, round both ends of the connector, to insure perfect tightness.

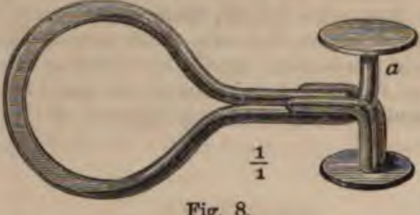

Fig. 8.

The space between the lower orifice of the burette and the upper orifice of the small delivery tube should be about 15 mm. The india-rubber tube is now pressed together between the ends of the tubes by the compression-cock (or clip). This latter instrument is usually made out of brass wire; the form represented in fig. 8 was given by Mohr.

A good clip must pinch so tight that not a particle of fluid can make its way through the connector when compressed by it; it must be so constructed that the analyst may work it with perfect facility and exactness, so as to regulate the outflow of the liquid with the most rigorous accuracy, by bringing a higher or less degree of pressure to bear upon it.

For supporting Mohr's burettes, I use the holder represented in fig. 7; this instrument, whilst securely confining the tube, permits its being moved up and down with perfect freedom, and also its being taken out, without interfering with the compression cock. The position of the burette must be strictly perpendicular, to insure which, care must be taken to have the grooves of the cork lining, which are intended to receive the tube, perfectly vertical, with the lower board of the stand in a horizontal position.

To charge the burette for a volumetrical operation, the point of the instrument is immersed in the liquid, the compression-cock opened, and a little liquid, sufficient at least to reach into the burette tube, sucked up by applying the mouth to the upper end; the cock is then closed, and the liquid poured into the burette until it reaches up to a little above the top mark. The burette having, if required, been duly adjusted in the proper vertical position, the liquid is allowed to drop out to the exact level of the top mark. The instrument is now ready for use. When as much liquid has flowed out as is required to attain the desired object, the analyst, before proceeding to read off the volume used, has to wait a few minutes, to give the particles of fluid adhering to the sides of the emptied portion of the tube proper time to run down. This is an indispensable part of the operation in accurate measurements, since, if neglected, an experiment in which the standard liquid in the burette is added slowly to the fluid under examination (in which, accordingly, the minute particles of fluid adhering to the glass have proper time afforded them during the operation itself to run down), will, of course, give slightly different results from those arrived at in another experiment, where the larger portion of the standard fluid is applied rapidly, and the last few drops alone are added slowly.

The *way* in which the *reading-off* is effected, is a matter of great importance in volumetric analysis; the first requisite is to bring the eye to a level with the top of the fluid. We must consequently settle the question—What is to be considered the top?

If you hold a burette, partly filled with water, between the eye and a strongly illumined wall, the surface of the fluid presents the appearance shown in fig. 10; if you hold close behind the tube a sheet of white paper, with a strong light falling on it, the surface of the fluid presents the appearance shown in fig. 9.

In the one as well as in the other case, you have to read off at the lower border of the dark zone, this being the most distinctly marked line. **Fr. Mohr** recommends the following device for reading-off:—Paste on a sheet of very white paper a broad strip of black paper, and, when reading-off, hold this close behind the burette, in a position to place the border line between white and black from 2 to 3 mm. below the lower border of the dark zone, as shown in fig. 11; read-off at the lower border of the dark zone.

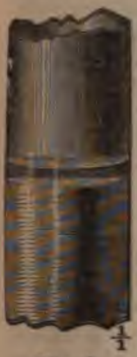

Fig. 9.

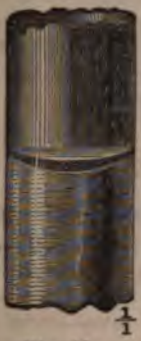

Fig. 10.

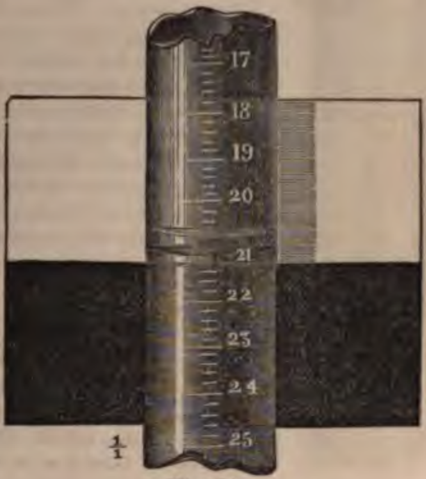

Fig. 11.

Great care must be taken to hold the paper invariably in the same position, since, if it be held lower down, the lower border of the black zone will move higher up.

I prefer to read-off in a light which causes the appearance represented in fig. 9.

By the use of **Erdmann**'s float * all uncertainties in reading-off may be avoided. Fig. 12 represents a burette thus provided. In this case we always read off the degree of the burette which coincides with the circle in the middle of the float. The float must be so fitted to the width of the burette that when placed in the filled burette, it will, on allowing the fluid to run out gradually, sink down with the same without wavering, and when it has been pressed down into the fluid of the closed burette, it will slowly rise again. The weight of the float must, if necessary, be so regulated by mercury that when placed in the filled tube it may cut the fluid with its top uniformly all round. A further important condition of the float is that its axis should coincide as nearly as possible with that of the burette tube, so that the division-mark on the burette may be always parallel with the circular line on the float.

The correctness of the graduation of a burette is tested in the most simple way, as follows: fill the instrument up to the highest division with water of 16°, then let 10 c. c. of the liquid flow out into an accurately weighed flask, and weigh; then let another quantity of 10 c. c. flow out, and weigh again, and repeat the operation until the contents of the burette are exhausted. If the instrument is correctly graduated, every 10 c. c. of water of 16° must weigh 9·990 grm. Differences up to 0·010 grm. may be disregarded, since even with the greatest care bestowed on the process of reading-off, deviations to that extent will occur in repeated measurements of the uppermost 10 c. c. of one and the same burette. With the float-burettes the weighings agree much more accurately, and the differences for 10 c. c. do not exceed 0·002 grm.

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* Journ. f. prakt. Chem. 71, 194.

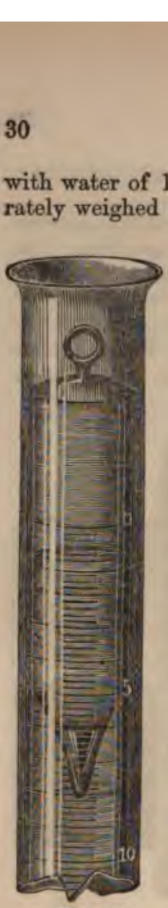

Fig. 12.

Mohr's burette is unquestionably the best and most convenient instrument of the kind, and ought to be employed in the measurement of all liquids which are not injuriously affected by contact with caoutchouc. Of the standard solutions used at present in volumetric analysis, that of permanganate of potassa alone cannot bear contact with caoutchouc.

§ 22.

II. *Gay-Lussac's Burette.*

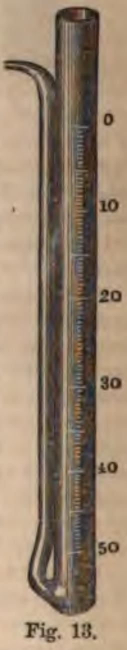

Fig. 13.

Fig. 13 represents this instrument in, as I believe, its most practical form.

I make use of two sizes, one of fifty c. c. divided into $\frac{1}{2}$ c. c., the other of 30 c. c. divided into $\frac{1}{10}$ c. c. The former is about 33 cm. long; the graduated portion occupies about 25 cm.; the internal diameter of the wide tube measures 15 mm.; that of the narrow tube 4 mm., which in the upper bent end gradually decreases to 2 mm. The graduated portion of the smaller burette is about 28 cm. long, and has accordingly an internal diameter of about 11 mm.

The stand which I make use of to rest my burettes in, consists of a disk of solid wood, from 5 to 6 cm. high, and from 10 to 12 cm. in diameter, with holes made with the auger and chisel, of proper size to receive the bottom part of the burettes.

To complete the instrument, **Mohr** suggests the use of a perforated cork, bearing a short glass tube bent at a right angle. The cork being inserted into the mouth of the wide tube, a piece of caoutchouc is drawn over the short glass tube; by blowing into this with greater or less force, the outflow of the liquid from the spout of the slightly slanting burette may be regulated at pleasure.

The reading-off of the height of the liquid is effected in the same way as explained in § 21. I prefer, however, placing the burette firmly against a perpendicular partition, either a strongly illumined door, or the pane of a window, to insure the vertical position of the instrument. It is only when operating with more highly concentrated, and accordingly opaque solutions of permanganate of potassa, that the method of reading off requires modification; in that case, the upper border of the liquid is noted; and the best way is to place the burette against a white background, and read off by reflected light.

§ 23.

III. *Geissler's Burette.*

In this instrument, which is represented in fig. 14, the narrow tube is placed inside the wide tube instead of outside, as in GAY-LUSSAC's burette. The part of the inner tube projecting beyond the wide tube is thick in the glass; whilst the part inside, which is of the same inside width, is made of very thin glass.

This is a very convenient instrument, and less liable to fracture than GAY-LUSSAC's burette.

II. PRELIMINARY OPERATIONS.—PREPARATION OF SUBSTANCES FOR THE PROCESSES OF QUANTITATIVE ANALYSIS.

§ 24.

1. THE SELECTION OF THE SAMPLE.

Before the analyst proceeds to make the quantitative analysis of a body, he cannot too carefully consider whether the desired result is fully attained if he simply knows the respective quantity of every individual constituent of that body. This primary point is but too frequently disregarded, and thus false impressions are made, even by the most careful analysis. This remark applies both to scientific and to technical investigations.

Therefore, if you have to determine the constitution of a mineral, take the greatest possible care to remove in the first place every particle of gangue, and disseminated impurities; remove any adherent matter by wiping or washing, then wrap the substance up in a sheet of thick paper, and crush it to pieces on a steel anvil; and pick out with a pair of small pincers the cleanest pieces. Crystalline substances, prepared artificially, ought to be purified by recrystallization; precipitates by thorough washing, &c., &c.

In technical investigations,—when called upon, for instance, to determine the amount of peroxide present in a manganese ore, or the amount of iron present in an iron ore,—the first point for consideration ought to be whether the samples selected correspond as much as possible to the average quality of the ore. What

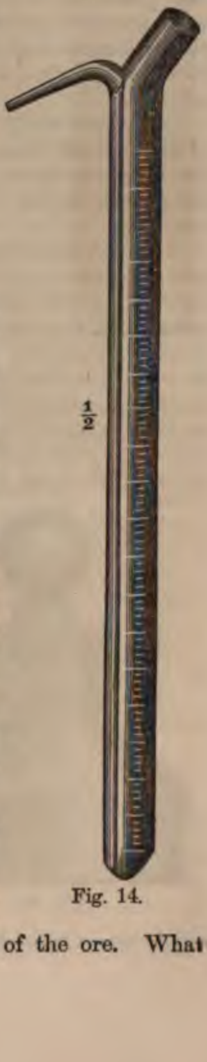

Fig. 14.

would it serve, indeed, to the purchaser of a manganese mine to know the amount of peroxide present in a select, possibly particularly rich, sample?

These few observations will suffice to show that no universally applicable and valid rules to guide the analyst in the selection of the sample can be laid down; he must in every individual case, on the one hand, examine the substance carefully, and more particularly also under the microscope, or through a lens; and, on the other hand, keep clearly in view the *object* of the investigation, and then take his measures accordingly.

§ 25.

2. MECHANICAL DIVISION.

In order to prepare a substance for analysis, *i.e.*, to render it accessible to the action of solvents or fluxes, it is generally indispensable, in the first place, to divide it into minute parts, since this will create abundant points of contact for the solvent, and will counteract, and, as far as practicable, remove the adverse influences of the power of cohesion, thus fulfilling all the conditions necessary to effect a complete and speedy solution.

The means employed to attain this object vary according to the nature of the different bodies we have to operate upon. In many cases, simple crushing or pounding is sufficient; in other cases it is necessary to reduce the powder to the very highest degree of fineness, by sifting or by elutriation.

The operation of powdering is conducted in mortars; the first and most indispensable condition is, that the material of the mortar be considerably harder than the substance to be pulverized, so as to prevent, as far as practicable, the latter from being contaminated with any particles of the former. Thus, for pounding salts and other substances possessing no very considerable degree of hardness, porcelain mortars may be used, whilst the pounding of harder substances (of most minerals, for instance,) requires vessels of agate, chalcedony, or flint. In such cases, the larger pieces are first reduced to a coarse powder; this is best effected by wrapping them up in several sheets of writing-paper, and striking them with a hammer upon a steel or iron plate; the coarse powder thus obtained is then pulverized, in small portions at a time, in an agate mortar, until it is reduced to the state of an impalpable powder. If we have but a small portion of a mineral to operate upon, and indeed in all cases where we are desirous of avoiding loss, it is advisable to use a steel mortar (fig. 15) for the preparatory reduction of the mineral to coarse powder.

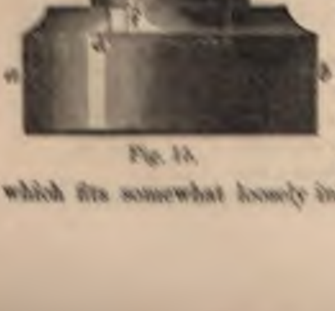

Fig. 15.

a b and *c d* represent the two parts of the mortar; these may be readily taken asunder. The substance to be crushed (having, if practicable, first been broken into small pieces), is placed in the cylindrical chamber *e f*; the steel cylinder, which fits somewhat loosely into the chamber, serves as pestle. The mortar is placed upon a solid support, and perpendicular blows are repeatedly struck upon the pestle with a hammer until the object in view is attained.

Minerals which are very difficult to pulverize should be strongly ignited, and then suddenly plunged into cold water, and subsequently again ignited. This process is of course applicable only to minerals which lose no essential constituent on ignition, and are perfectly insoluble in water.

In the purchase of agate mortars, especial care ought to be taken that they have no palpable cracks or indentations; very slight cracks, however, that cannot be felt, do not render the mortar useless, although they impair its durability.

Minerals insoluble in acids, and which consequently require fusing, must especially be finely divided, otherwise we cannot calculate upon complete decomposition. This object may be obtained either by triturating the pounded mineral with water, or by elutriation, or by sifting; the two former processes, however, can be resorted to only in the case of substances which are not attacked by water. It is quite clear that analysts must in future be much more cautious in this point than has hitherto been the case, since we know now that many substances which are usually held to be insoluble in water are, when in a state of minute division, strongly affected by that solvent; thus, for instance, water, acting upon some sorts of finely pulverized glass, is found to rapidly dissolve from 2 to 3 per cent. of the powder even in the cold. (PELOUZE.[*]) Thus, again, finely divided feldspar, granite, trachyte and porphyry give up to water both alkali and silica. (H. LUDWIG.[†])

Trituration with water (levigation). Add a little water to the pounded mineral in the mortar, and triturate the paste until all crepitation ceases, or, which is a more expeditious process, transfer the mineral paste from the mortar to an agate or flint slab, and triturate it thereon with a muller. Rinse the paste off, with the washing bottle, into a smooth porcelain basin of hemispheric form, evaporate the water on the water-bath, and mix the residue most carefully with the pestle. (The paste may be dried also in the agate mortar, but at a very gentle heat, since otherwise the mortar might crack.)

To perform the process of *elutriation*, the pasty mass, having first been very finely triturated with water, is washed off into a beaker, and stirred with distilled water; the mixture is then allowed to stand a minute or so, after which the supernatant turbid fluid is poured off into another beaker. The sediment, which contains the coarser parts, is then again subjected to the process of trituration, &c., and the same operation repeated until the whole quantity is elutriated. The turbid fluid is allowed to stand at rest until the minute particles of the substance held in suspension have subsided, which generally takes many hours. The water is then finally decanted, and the powder dried in the beaker.

The process of *sifting* is conducted as follows: a piece of fine, well-washed, and thoroughly dry linen is placed over the mouth of a bottle about 10 cm. high, and pressed down a little into the mouth, so as to form a kind of bag; a portion of the finely triturated substance is put into the bag, and a piece of soft leather stretched tightly over the top by way of cover. By drumming with the finger on the leather cover, a shaking motion is imparted to the bag, which makes the finer particles of the powder gradually pass through the linen. The portion remaining in the bag is subjected again to trituration in an agate mortar, and, together with a fresh portion of the powder, sifted again; and the same process is continued until the entire mass has passed through the bag into the glass.

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[*] Compt. Rend. t. xliii., pp. 117–123.
[†] Archiv der Pharm. 91, 147.

When operating on substances consisting of different compounds it would be a grave error indeed to use for analysis the powder resulting from the first process of elutriation or sifting, since this will contain the more readily pulverizable constituents in a greater proportion to the more resisting ones than is the case with the original substance.

Great care must, therefore, also be taken to avoid a loss of substance in the process of elutriation or sifting, as this loss is likely to be distributed unequally among the several component parts.

In cases where it is intended to ascertain the average composition of a heterogeneous substance, of an iron ore for instance, a large average sample is selected, and reduced to a coarse powder; the latter is thoroughly intermixed, a portion of it powdered more finely, and mixed uniformly, and finally the quantity required for analysis is reduced to the finest powder. The most convenient instrument for the crushing and coarse pounding of large samples of ore, &c., is a steel anvil and hammer. The anvil in my own laboratory consists of a wood pillar, 85 cm. high and 26 cm. in diameter, into which a steel plate, 3 cm. thick and 20 cm. in diameter, is let to the depth of one-half of its thickness. A brass ring, 5 cm. high, fits round the upper projecting part of the steel plate. The hammer, which is well steeled, has a striking surface of 5 cm. diameter. An anvil and hammer of this kind afford, among others, this advantage, that their steel surfaces admit most readily of cleaning. To convert the coarse powder into a finer, a smooth-turned steel mortar of about 130 mm. upper diameter and 74 mm. deep is used—the final trituration is conducted in an agate mortar.

§ 27.

3. DRYING.

Bodies which it is intended to analyze quantitatively, must be, when weighed, in a definite state, in a condition in which they can be always obtained again.

Now, the essential constituents of a substance are usually accompanied by an unessential one, viz., a greater or less amount of water, enclosed either within its lamellæ, or adhering to it from the mode of its preparation, or absorbed by it from the atmosphere. It is perfectly obvious that to estimate correctly the quantity of a substance, we must, in the first place, remove this variable amount of water. Few solid bodies, therefore, require to be dried before they can be quantitatively analyzed.

The operation of drying is of the very highest importance for the correctness of the results; indeed it may safely be asserted that many of the differences observed in analytical researches proceed merely from the fact that substances are analyzed in different states of moisture.

Many bodies contain, as is well known, water which is proper to them either as essential to their constitution or as so-called water of crystallization. In contradistinction to this, we will employ the term *moisture* to designate that variable adherent or mechanically enclosed water, with the removal of which the operation of drying in the sense here in view is alone concerned.

In the drying of substances for quantitative analysis, our object is to remove all moisture, without interfering in the slightest degree with combined water or any other constituent of the body. To accomplish this object, it is absolutely requisite that we should know the properties which the substance under examination manifests in the dry state, and whether it loses water or other constituents at a red heat, or at 100°, or in dried air, or even simply in contact with the atmosphere. These data will serve to guide us in the selection of the process of desiccation best suited to each substance.*

The following classification may accordingly be adopted:—

a. Substances which lose water even in simple contact with the atmosphere; such as sulphate of soda, crystallized carbonate of soda, &c. Substances of this kind turn dull and opaque when exposed to the air, and finally crumble wholly or partially to a white powder. They are more difficult to dry than many other bodies. The process best adapted for the purpose, is to press the pulverized salts with some degree of force between thick layers of fine white blotting-paper, repeating the operation with fresh paper until the last sheets remain *absolutely dry.*

It is generally advisable in the course of this operation to repowder the salt.

b. Substances which do not yield water to the atmosphere (unless it is perfectly dry), but effloresce in artificially dried air; such as sulphate of magnesia, tartrate of potassa and soda (Rochelle salt), &c. Salts of this kind are reduced to powder, which, if it be very moist, is pressed between sheets of blotting paper, as in *a*; after this operation, it must be allowed to remain for some time spread in a thin layer upon a sheet of blotting-paper, effectually protected against dust, and shielded from the direct rays of the sun.

§ 27.

c. Substances which undergo no alteration in dried air, but lose water at 100°; tartrate of lime, for instance. These are finely pulverized; the powder is put in a thin layer into a watch-glass or shallow dish, and the latter placed inside a chamber in which the air is kept dry by means of sulphuric acid. This process is usually conducted in one of the following apparatuses, which are termed *desiccators*, and subserve still another purpose besides that of drying, viz., that of allowing hot crucibles, dishes, &c., to cool in dry air.

In fig. 16, *a* represents a glass plate (ground-glass plates answer the purpose best), *b*, a bell jar with ground rim, which is greased with tallow; *c* is a glass basin with sulphuric acid; *d*, a round iron plate, supported on three feet, with circular holes of various sizes, for the reception of the watch-glasses, crucibles, &c., containing the substance.

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* The dried substance should always at once be transferred to a well-closed vessel; glass tubes, sealed at one end, and of sufficiently thick glass to bear the firm insertion of tight-fitting smooth corks—weighing-tubes—are usually employed for this purpose.

In fig. 17, *a* represents a beaker with ground and greased rim, and filled to one-fourth or one-third with concentrated sulphuric acid; *b* is a ground-glass plate; *c* is a bent wire of lead, which serves to support the watch-glass containing the substance.

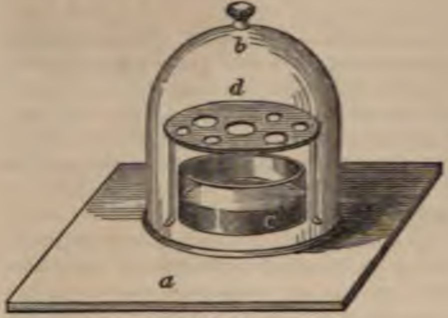

Fig. 16.

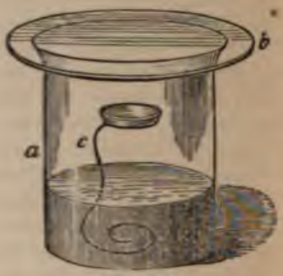

Fig. 17.

Fig. 18 represents a readily portable desiccator, used more particularly to receive crucibles in course of cooling, and carry them to the balance. The instrument consists of a box made of strong glass; the lid must be ground to shut air-tight; the place on which it joins is greased with tallow. The outer diameter of my boxes is 105 mm.; the sides are 6 mm. thick. The aperture has a diameter of 80 mm.; the box up to the small part is 65 mm. high; the lid has the same height; the small part itself is 15 mm. high, and ground to a slightly conical shape. A brass ring, with rim, fits exactly into the aperture; the rim must not project beyond the glass. The ring bears a triangle of iron, or, better, platinum wire, intended for the reception of crucibles, &c.

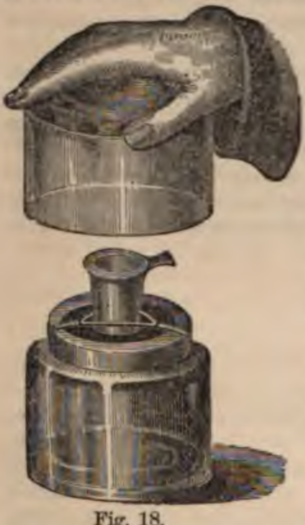

Fig. 18.

The body which it is intended to dry is kept exposed to the action of the dry air in the glass, until it shows no further diminution of weight. Substances upon which the oxygen of the air exercises a modifying influence are dried in a similar manner, under the exhausted receiver of an air-pump. Substances which, though losing no water in dry air, yet give off ammonia, are dried over quicklime, mixed with some chloride of ammonium in powder, and consequently in an anhydrous ammoniacal atmosphere.

§ 28.

d. Substances which at 100° *completely lose their moisture, without suffering any other alteration*, such as bitartrate of potassa, sugar, &c. These are dried in the water-bath; in the case of slow-drying substances, or where it is wished to expedite the operation, with the aid of a current of dry air.

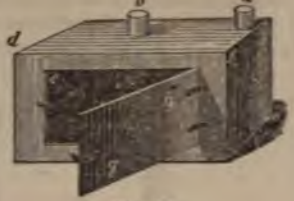

Fig. 19.

Fig. 19 represents the water-bath most commonly used. It is made of sheet copper. The engraving renders a detailed description unnecessary. The inner chamber, c, is surrounded on five sides by the outer case or jacket, *d e*, without communicating with it. The object of the apertures *g* and *h* is to effect change of air, which purpose they answer sufficiently well. When it is intended to use the apparatus, the outer case is filled to about one-half with rain-water, and the aperture *a* is closed with a perforated cork, into which a glass tube is fitted; the aperture *b* is entirely closed. If the apparatus is intended to be heated over charcoal, it should have a length of about 20 cm. from *d* to *f*; but if over a gas-, spirit-, or oil-lamp, it should be only about 13 cm. long. In the former case, the inner chamber is 17 cm. deep, 14 cm. broad, and 10 cm. high; in the latter case, it is 10 cm. deep, 9 cm. broad, and 6 cm. high. The temperature in the inner chamber never quite reaches 100°; to bring it up to 100°, F. ROCHLEDER has suggested to close *b* with a double-limbed tube, the outer longer limb of which dips into a cylinder filled with water; *a* is in that case closed with a perforated cork bearing a sufficiently tall funnel tube, which fits air-tight in the cork. The lower end of this tube reaches down to one inch from the bottom.

In large analytical laboratories water is usually kept boiling all day long, for the production of distilled water. The boilers used in my own laboratory have the shape of somewhat oblong square boxes, about 120 cm. long, 60 cm. broad, and 24 cm. high; the front of the boiler has soldered into it, one above the other, two rows of drying chambers, of the kind shown in fig. 19. This gives so many ovens that almost every student may have one for his special use. Most of these ovens are from 11 to 12 cm. deep and broad, and 8 cm. high; some of them, however, are 16 cm. deep and broad, to enable them to receive large-sized dishes. The substances to be dried are usually put on double watch-glasses, laid one within the other, which are placed in the oven, and the door is then closed. In the subsequent process of weighing, the upper glass, which contains the substance, is covered with the lower one. The glasses must be quite cold before they are placed on the scale. In cases where we have to deal with hygroscopic substances, the reabsorption of water upon cooling is prevented by the selection of close-fitting glasses, which are held tight together by a clasp (fig. 20), and allowed to cool with their contents under a bell-glass over sulphuric acid (see fig. 16). These latter instructions apply equally to the process of drying conducted in other apparatus.

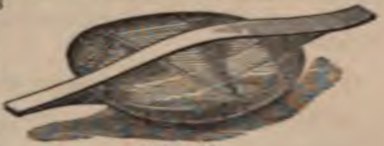
Fig. 20.

The clasp used for keeping the watch-glasses pressed together—and which in all cases where it is intended to ascertain the loss of weight which a substance suffers on desiccation, is to be looked upon as belonging to the glasses, and must accordingly be ings, so that it shall traverse the chamber and project 40–50 mm. beyond the corks at each end. The copper tubes should be so adjusted that the glass tube shall stand horizontally in the chamber, at the same height as the thermometer bulb and just behind it. To produce the current of dry air one of the projecting ends of the wide tube is connected by a narrow glass tube and perforated cork, with an aspirator as in fig. 21, the other with a large chloride of calcium tube; the water of the aspirator is allowed to run off somewhat rapidly at first, more slowly afterwards. The end of the tube that delivers the air into the wide tube is recurved, so that the substance within shall not be carried away in the current.

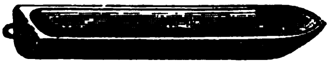

Fig. 24.

The substance to be dried is weighed out in a tray of platinum or porcelain, fig. 24, which is pushed within the wide glass tube by help of a wire. When the substance is hygroscopic, the tray is placed horizontally within a test-tube, which is corked while the weight is being ascertained. The substance and tray, after drying, may be cooled in the same test-tube; in that case, just before putting on the balance, the cork should be removed momentarily to allow the tube to fill with air.]

§ 30.

The copper apparatus represented in fig. 19, when made with brazed joints, can be employed also as a paraffine-bath; when used for that purpose, the outer case is filled to two-thirds with paraffine. To note the temperature, a thermometer is inserted, by means of a perforated cork, in the aperture *a*; with the bulb reaching nearly to the bottom, or, at all events, entirely immersed in the paraffine.

Many organic substances, when dried at a somewhat high temperature, suffer alteration by the action of the atmospheric oxygen. In the desiccation of such substances, oxygen must accordingly be excluded.

[The drying of such bodies is conducted as just described in the modified air-bath, but in a stream of dried and purified hydrogen or carbonic acid (see §29). The gas is evolved from a self-regulating generator (see fig. 47, § 108, or "Qual. Anal.," Am. ed. p. 49). To the end of the wide tube from which the gas escapes is fitted a perforated cork and long narrow tube.]

§ 31.

f. Substances which suffer no alteration at a red heat, such as sulphate of baryta, pearlash, &c., are very readily freed from moisture. They need simply be heated in a platinum or porcelain crucible over a gas or spirit-lamp until the desired end is attained. The crucible, having first been allowed to cool a little, is put, still hot, under a desiccator, and finally weighed when cold.

III. GENERAL PROCEDURE IN QUANTITATIVE ANALYSES.

§ 32.

It is important, in the first place, to observe that we embrace in the following general analytical method only the separation and determination of the metals and their combinations with the metalloids, and of the inorganic acids and salts. With respect to the quantitative analysis of other compounds, it is not easy to lay down a universally applicable method, except that their constituents usually require to be converted first into acids or bases, before their separation and estimation can be attempted; this is the case, for instance, with sulphide of phosphorus, chloride of sulphur, chloride of iodine, sulphide of nitrogen, &c.

The quantitative analysis of a substance presupposes an accurate knowledge of the properties of the same, and of the nature of its several constituents. These data will enable the operator at once to decide whether the direct estimation of each individual constituent is necessary; whether he need operate only on one portion of the substance, or whether it would be advantageous to determine each constituent in different portions. Let us suppose, for instance, we have a mixture of chloride of sodium and anhydrous sulphate of soda, and wish to ascertain the proportion in which these two substances are mixed. Here it would be superfluous to determine each constituent directly, since the determination either of the quantity of the chlorine, or of the sulphuric acid, is quite sufficient to answer the purpose; still the estimation of both the chlorine and the sulphuric acid will afford us an infallible control for the correctness of our analysis; since the united weights of these two substances, added to the sodium and soda respectively equivalent to them, must be equal to the weight of the substance taken.

These estimations may be made, either in one and the same portion of the mixture, by first precipitating the sulphuric acid with nitrate of baryta, and subsequently the hydrochloric acid from the filtrate with solution of nitrate of silver; or a separate portion of the mixture may be appropriated to each of these two operations. Unless there is some objection to its use (*e.g.*, deficiency or heterogeneousness of substance), the latter method is more convenient and generally yields more accurate results; since, in the former method, the unavoidable washing of the first precipitate swells the amount of liquid so considerably that the analysis is thereby delayed, and, moreover, loss of substance less easily guarded against.

Before beginning all analyses, at least those of a more complex nature, the student should write out an exact plan, and accurately note on paper, during the entire process, everything that he does. It is in the highest degree unwise to rely on the memory in a complicated analysis. When students, who imagine they can do so, come, a week or a fortnight after they have begun their analysis, to work out the results, they find generally too late that they have forgotten much, which now appears to them of importance to know. The intelligent pursuit of chemical analysis consists in the projecting and accurate testing of the plan; acuteness and the power of passing in review all the influencing chemical relations must here support each other. He who works without a thoroughly thought-out plan, has no right to say he is practising chemistry; for a mere unthinking stringing together of a series of filtrations, evaporations, ignitions, and weighings, howsoever well these several operations may be performed, is not chemistry.

We will now proceed to describe the various operations constituting the process of quantitative analysis.

§ 33.

1. WEIGHING THE SUBSTANCE.

The amount of matter required for the quantitative analysis of a substance depends upon the nature of its constituents; it is, therefore, impossible to lay down rules for guidance on this point. Half a gramme of chloride of sodium, and even less, is sufficient to effect the estimation of the chlorine. For the quantitative analysis of a mixture of common salt and anhydrous sulphate of soda, 1 gramme will suffice; whereas, in the case of ashes of plants, complex minerals, &c., 3 or 4 grammes, and even more, are required. 1 to 3 grm. can therefore be indicated as the average quantity suitable in most cases. For the estimation of constituents present in very minute proportions only, as, for instance, alkalies in limestones, phosphorus or sulphur in cast-iron, &c., much greater quantities are often required—10, 20, or 50 grammes.

The greater the amount of substance taken the more accurate will be the analysis; the smaller the quantity, the sooner, as a rule, will the analysis be finished. We would advise the student to endeavor to combine accuracy with economy of time. The less substance he takes to operate upon, the more carefully he ought to weigh; the larger the amount of substance, the less harm can result from slight inaccuracies in weighing. Somewhat large quantities of substance are generally weighed to 1 milligramme; minute quantities, to $\frac{1}{10}$ of a milligramme.

If *one* portion of a substance is to be weighed off, we first weigh two watch-glasses which fit on each other, or else an empty platinum crucible with lid, then we put some substance in, and weigh again; the difference between the two weighings gives the weight of the substance taken.

If *several* quantities of a substance are to be operated upon, the best way is to weigh off the several portions successively; which may be accomplished most readily by weighing in a glass tube, or other appropriate vessel, the whole amount of substance, and then shaking out of the tube the quantities required one after another into appropriate vessels, weighing the tube after each time.

The work may often also be materially lightened, by weighing off a larger portion of the substance, dissolving this to $\frac{1}{4}$, $\frac{1}{2}$ or 1 litre, and taking out for the several estimations aliquot parts, with the 50 or 100 c. c. pipette. The first and most essential condition of this proceeding, of course, is that the pipettes must accurately correspond with the measuring flasks (§§ 18 and 20).

§ 34.

2. Estimation of the Water.

If the substance to be examined—after having been freed from moisture by a suitable drying process (§§ 26—32)—contains water, it is usual to begin by determining the amount of this water. This operation is generally simple; in some instances, however, it has its difficulties. This depends upon various circumstances, viz., whether the compounds intended for analysis yield their water readily or not; whether they can bear a red heat without suffering decomposition; or whether, on the contrary, they give off other volatile substances, besides water, even at a lower temperature.

The correct knowledge of the constitution of a compound depends frequently upon the accurate estimation of the water contained in it; in many cases—for instance, in the analysis of the salts of known acids—the estimation of the water contained in the analyzed compound suffices to enable us to deduce the formula. The estimation of the water contained in a substance is, therefore, one of the most important, as well as most frequently occurring operations of quantitative analysis. The proportion of water contained in a substance may be determined in two ways, viz., *a*, from the diminution of weight consequent upon the expulsion of the water; *b*, by weighing the amount of water expelled.

§ 35.

a. ESTIMATION OF THE WATER FROM THE LOSS OF WEIGHT.

This method, on account of its simplicity, is most frequently employed. The *modus operandi* depends upon the nature of the substance under examination.

α. *The Substance bears ignition without losing other Constituents besides Water, and without absorbing Oxygen.*

The substance is weighed in a platinum or porcelain crucible, and placed over the gas or spirit lamp; the heat should be very gentle at first, and gradually increased. When the crucible has been maintained some time at a red heat, it is allowed to cool a little, put still warm under the desiccator, and finally weighed when cold. The ignition is then repeated, and the weight again ascertained. If no further diminution of weight has taken place, the process is at an end, the desired object being fully attained. But if the weight is less than after the first heating, the operation must be repeated until the weight remains constant.

In the case of silicates, the heat must be raised to a very high degree, since many of them (*e.g.* talc, steatite, nephrite) only begin at a red heat to give off water, and require a yellow heat for the complete expulsion of that constituent. (TH. SCHEERER.*) Such bodies are therefore ignited over a blast lamp.

In the case of substances that have a tendency to puff off, or to spirt, a small flask or retort may sometimes be advantageously substituted for the crucible. Care must be taken to remove the last traces of aqueous vapor from the vessel, by suction through a glass tube.

Decrepitating salts (chloride of sodium, for instance) are put—finely pulverized, if possible—in a small covered platinum crucible, which is then placed in a large one, also covered; the whole is weighed, then heated, gently at first for some time, then more strongly; finally, after cooling, weighed again.

β. *The substance loses on ignition other Constituents besides Water (Boracic Acid, Sulphuric Acid, Fluoride of Silicon, &c.).*

Here the analyst has to consider, in the first place, whether the water may not be expelled at a lower degree of heat, which does not involve the loss of other constituents. If this may be done, the substance is heated either in the water-bath, or where a higher temperature is required, in the air-bath or oil-bath, the temperature being regulated by the thermometer. The expulsion of the water may be promoted by the co-operation of a current of air (compare §§ 29 and 30); or by the addition of pure dry sand to the substance, to keep it porous.† The process must be continued under these circumstances also, until the weight remains constant.

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* Jahresber. von Liebig u. Kopp, 1851, 610.

† Ann. d. Chem. u. Pharm., 53, 233.

In cases where, for some reason or other, such gentle heating is insufficient, the analyst has to consider whether the desired end may not be attained at a red heat, by adding some substance that will retain the volatile constituent whose loss is apprehended. Thus, for instance, the crystallized sulphate of alumina loses at a red heat, besides water, also sulphuric acid; now, the loss of the latter constituent may be guarded against by adding to the sulphate an excess (about six times the quantity) of finely pulverized, recently ignited, pure oxide of lead. But the addition of this substance will not prevent the escape of fluoride of silicon from silicates when exposed to a red heat (LIST *).

Thus again, the amount of water in commercial iodine may be determined by triturating the iodine together with eight times the quantity of mercury, and drying the mixture at 100° (BOLLEY†).

γ. *The Substance contains several differently combined quantities of Water which require different Degrees of Temperature for Expulsion.*

Substances of this nature are heated first in the water-bath, until their weight remains constant; they are then exposed in the oil- or air-bath to 150, 200, or 250°, &c., and finally, when practicable, ignited over a gas- or spirit-lamp. [In such experiments, it is best to proceed as described, § 29, p. 39, viz., to heat in a current of dried air, hydrogen, or carbonic acid.]

In this manner differently combined quantities of water may be distinguished, and their respective amounts correctly estimated. Thus, for instance, crystallized sulphate of copper contains 28·87 per cent. of water, which escapes at a temperature below 140°, and 7·22 per cent., which escapes only at a temperature between 220 and 260°.

δ. *When the substance has a tendency to absorb oxygen* (from the presence of protoxide of iron, for instance) the water is better determined in the direct way, than by the loss. (§ 36.)

§ 36.

b. ESTIMATION OF WATER BY DIRECT WEIGHING.

This method is resorted to by way of control, or in the case of substances which, upon ignition, lose, besides water, other constituents, which cannot be retained even by the addition of some other substance (*e.g.*, carbonic acid, oxygen), or in the case of substances containing bodies inclined to oxidation (*e.g.*, protoxide of iron). The principle of the method is to expel the water by the application of a red heat, so as to admit of the condensation of the aqueous vapor, and the collection of the condensed water in an appropriate apparatus, partly physically, partly by the agency of some hygroscopic substance. The increase in the weight of this apparatus represents the quantity of the water expelled.

The operation may be conducted in various ways; the following is one of the most appropriate :—

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* Ann. d. Chem. u. Pharm., 81, 189.

† Dingler's Polyt. Journ., 126, 39.

B, fig. 25, represents a gasometer filled with air; *b* a flask half-filled with concentrated sulphuric acid; *c* and *a o* are chloride of calcium tubes; *d* is a bulb-tube.

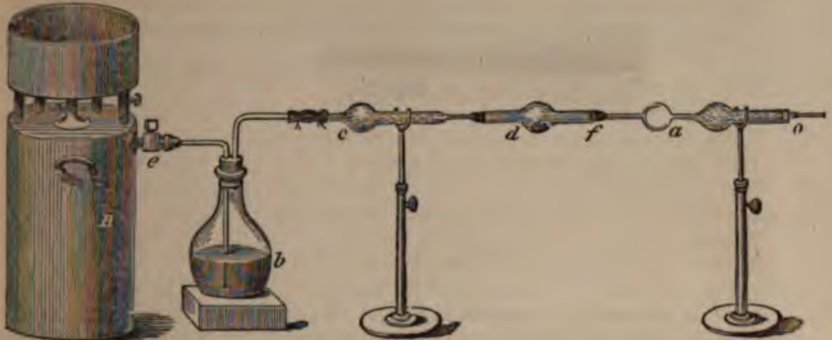

Fig. 25.

The substance intended for examination is weighed in the perfectly dry tube *d*,* which is then connected with *c* and the weighed chloride of calcium tube *a o*, by means of sound and well-dried perforated corks.

The operation is commenced by opening the stop-cock *e* a little, to allow the air, which loses all its moisture in *b* and *c*, to pass slowly through *d*; the tube *d* is then heated to beyond the boiling-point of water, by holding a lamp towards *f*, taking care not to burn the cork; and finally, the bulb which contains the substance is exposed to a low red heat, the temperature at *f* being maintained all the while at the point indicated. When the expulsion of the water has been accomplished, a slow current of air is still kept up till the bulb-tube is cold; the apparatus is then disconnected, and the chloride of calcium tube *a o*, weighed. The increase in the weight of this tube represents the quantity of water originally present in the substance examined.

The empty bulb *a*, in which the greater portion of the water collects, has not only for its object to prevent the liquefaction of the chloride of calcium, but enables the analyst also to test the condensed water as to its reaction and purity.

The apparatus may, of course, be modified in various ways; thus, the chloride of calcium tubes may be U-shaped; a U-tube, filled with pieces of pumice-stone saturated with sulphuric acid, may be substituted for the flask with sulphuric acid; and the gasometer may be replaced by an aspirator (fig. 21) joined to *o*.

The expulsion of the aqueous vapor from the tube containing the substance under examination, into the chloride of calcium tube, may be effected also by other means than a current of air supplied by a gasometer or aspirator; viz., the substance under examination may be heated to redness in a perfectly dry tube, together with carbonate of lead, since the carbonic acid of the latter, escaping at a red heat, serves here the same purpose as a stream of air. This method is principally applied in cases where it is desirable to retain an acid which otherwise would volatilize together with the water; thus, it is applied, for instance, for the direct estimation of the water contained in the bisulphate of potassa, &c.

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* **[It is usually better to weigh off the substance into a tray or boat of porcelain or platinum, and place this within a straight tube of hard glass and ignite by means of a tube furnace.]**

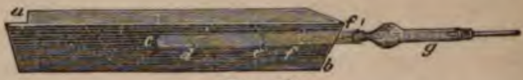

Fig. 26.

Fig. 26 represents the disposition of the apparatus.

a b is a common combustion furnace; *c* f'' a tube filled as follows:—from *c* to *d* with carbonate of lead,* from *d* to *e* the substance intimately mixed with carbonate of lead, and from *e* to *f* pure carbonate of lead. The chloride of calcium tube *g*, being accurately weighed, is connected with the tube *c* f'', by means of a well-dried perforated cork, f'.

The operation is commenced by surrounding the tube with red-hot charcoal, advancing from f'' toward *c*; the fore part of the tube which protrudes from the furnace should be maintained at a degree of heat which barely permits the operator to lay hold of it with his fingers. All further particulars of this operation will be found in the chapter on organic elementary analysis. The mixing is performed best in the tube with a wire. The tube *c* f'' may be short and moderately narrow.

The volatilization of an acid cannot in all cases be prevented by oxide of lead; thus, for instance, we could not determine the water in crystallized boracic acid by the above process. This could readily be done, however, by igniting the acid mixed with excess of dry carbonate of soda in a glass tube drawn out behind in the form of a beak, receiving the water in a chloride of calcium tube, and transferring the final residue of aqueous vapor into the Ca Cl-tube by suction, after the point of the beak has been broken off. (See Organic Analysis.)

The foregoing methods for the direct estimation of water do not, however, yet embrace all cases in which those described in § 35 are inapplicable; since they can be employed only if the substances escaping along with the water are such as will not wholly or partly condense in the chloride of calcium tube (or in a hydrate of potassa tube, or one filled with pumice-stone saturated with sulphuric acid, which might be used instead). Thus they are perfectly well adapted for determining the water in the basic carbonate of zinc, but they cannot be applied to determine the water in sulphate of soda and ammonia. With substances like the latter, we must either have recourse to the processes of organic elementary analysis, or we must rest satisfied with the indirect estimation of the water.

§ 37.

3. Solution of Substances.

Before pursuing the analytical process further, it is in most cases necessary to obtain a solution of the substance. This operation is simple where the body may be dissolved by direct treatment with water, or acids, or alkalies, &c.; but it is more complicated in cases where the body requires fluxing as an indispensable preliminary to solution.

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* The carbonate of lead must have been previously ignited to incipient decomposition, and cooled in a closed tube.

When we have mixed substances to operate upon, the component parts of which behave differently with solvents, it is not by any means necessary to dissolve the whole substance at first; on the contrary, the separation may, in such cases, be often effected, in the most simple and expeditious manner, by the solvents themselves. Thus, for instance, a mixture of nitrate of potassa, carbonate of lime, and sulphate of baryta, may be readily and accurately analyzed by dissolving out, in the first place, the nitrate of potassa with water, and subsequently the carbonate of lime by hydrochloric acid, leaving the insoluble sulphate of baryta.

§ 38.

a. DIRECT SOLUTION.

The direct solution of substances is effected, according to circumstances, in beakers, flasks, or dishes, and may, if necessary, be promoted by the application of heat; for which purpose the water-bath will be found most convenient. In cases where an open fire, or the sand-bath, or an iron-plate is resorted to, the analyst must take care to guard against actual ebullition of the fluid, since this would render a loss of substance from spirting almost unavoidable, especially in cases where the process is conducted in a dish. Fluids containing a sediment, either insoluble, or, at least, not yet dissolved, will, when heated over the lamp, often bump and spirt even at temperatures far short of the boiling-point.

In cases where the solution of a substance is attended with evolution of gas, the process is conducted in a flask, placed in a sloping position, so that the spirting drops may be thrown against the walls of the vessel, and thus secured from being carried off with the stream of the evolved gas; or it may be conducted in a beaker, covered with a large-sized watch-glass, which, after the solution is effected, and the gas expelled by heating on the water-bath, must be thoroughly rinsed with the washing-bottle.

In cases where the solution has to be effected by means of concentrated volatile acids (hydrochloric acid, nitric acid, aqua regia), the operation should never be conducted in a dish, but always in a flask covered with a watch-glass, or placed in a slanting position, and the application of too high a temperature must be avoided. The operation should always be conducted also under a hood, with proper draught, to carry off the escaping acid vapors. In my own laboratory, I use for the latter purpose the following simple contrivance: a leaden pipe, permanently fixed in a convenient position, leads from the working table through the wall or the window-frame into the open air. The end in the laboratory is connected with one of the mouths of a two-necked bottle which contains a little water. The other mouth of the bottle is closed with a perforated cork, bearing a firmly-fixed glass tube bent at a right angle; the portion of the tube which enters the bottle must not dip into the water. The solution-flask being now closed with a perforated cork, or an india-rubber cap, bearing a glass tube, connected by means of india-rubber with the bent tube in the doubled-necked bottle, the vapors evolved are carried out of the laboratory without the least inconvenience to the operator; moreover, no receding of fluid upon cooling need be apprehended. Instead of conveying the vapors away through a tube leading into the open air, a conical glass-tube filled with pieces of broken glass, moist oned with water or solution of carbonate of soda, may be fixed on the second mouth of the double-necked bottle. I, however, prefer the other method. In some cases, it is advisable also to conduct the escaping vapors into a little water, and, when solution has been effected, make the water recede by withdrawing the lamp, since this will, at the same time, serve to dilute the solution; care must be taken, however, to guard against a premature receding of the water in consequence of an accidental cooling of the solution flask.

It is often necessary, in conducting a process of solution, to guard against the action of the atmospheric oxygen; in such cases, a slow stream of carbonic acid is transmitted through the solution-flask; in some cases it is sufficient to expel the air, by simply first putting a little bicarbonate of soda into the flask, containing an excess of acid, before introducing the substance.

§ 39.

b. SOLUTION, PRECEDED BY FLUXING.

Substances insoluble in water, acids, or aqueous alkalies, usually require decomposition by fluxing, to prepare them for analysis. Substances of this kind are often met with in the mineral kingdom; most silicates, the sulphates of the alkaline earths, chrome ironstone, &c., belong to this class.

The object and general features of the process of fluxing have already been treated of in the qualitative part of the present work. The special methods of conducting this important operation will be described hereafter under "The analysis of silicates," and in the proper places; as a satisfactory description of the process, with its various modifications, cannot well be given without entering more minutely into the particular circumstances of the several special cases.

Decomposition by fluxing often requires a higher temperature than is attainable with a spirit-lamp with double draught, or with a common gas lamp. In such cases, the glass-blower's lamp, fed with gas, is used with advantage.

§ 40.

4. CONVERSION OF THE DISSOLVED SUBSTANCE INTO A WEIGHABLE FORM.

The conversion of a substance in a state of solution into a form adapted for weighing may be effected either by *evaporation* or by *precipitation*. The former of these operations is applicable only in cases where the substance the weight of which we are desirous to ascertain, either exists already in the solution in the form suitable for the determination of its weight, or may be converted into such form by evaporation in conjunction with some reagent. The solution must, moreover, contain the substance unmixed, or, at least, mixed only with such bodies as are expelled by evaporation or at a red heat. Thus, for instance, the amount of sulphate of soda present in an aqueous solution of that substance may be ascertained by simple evaporation; whilst the carbonate of potassa contained in a solution would better be converted into chloride of potassium, by evaporating with solution of chloride of ammonium.

Precipitation may always be resorted to, whenever the substance in solution admits of being converted into a combination which is insoluble in the menstruum present, provided that the precipitate is fit for determination, which can never be the case unless it can be washed and is of constant composition.

§ 41.

a. EVAPORATION.

In processes of evaporation for pharmaceutical or technico-chemical purposes the principal object to be considered is saving of time and fuel; but in evaporating processes in quantitative analytical researches this is merely a subordinate point, and the analyst has to direct his principal care and attention to the means of guarding against loss or contamination of the substance operated upon.

The simplest case of evaporation is when we have to *concentrate a clear fluid, without carrying the process to dryness.* To effect this object, the fluid is poured into a basin, which should not be filled to more than two-thirds. Heat is then applied by placing the basin either on a water-bath, sand-bath, common stove, or heated iron plate, or over the flame of a gas- or spirit-lamp, care being taken always to guard against actual ebullition, as this invariably and unavoidably leads to loss from small drops of fluid spirting out. Evaporation over a gas or spirit-lamp, when conducted with proper care, is an expeditious and cleanly process. BUNSEN's gas-lamp may be used most advantageously in operations of this kind; a little wire-gauze cap, loosely fitted upon the tube of the lamp, is a material improvement. By means of this simple arrangement it is easy to produce even the smallest flame, without the least apprehension of ignition of the gas within the tube.

If the evaporation is to be effected on the water-bath, and the operator happens to possess a BEINDORF, or other similarly-constructed steam apparatus, the evaporating-dish may be placed simply into an opening corresponding in size. Otherwise recourse must be had to the water-bath, illustrated by fig. 27.

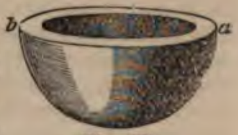

Fig. 27.

It is made of strong sheet copper, and when used is half filled with water, which is kept boiling over a gas-, spirit-, or oil-lamp. The breadth from *a* to *b* should be from 12 to 18 cm. Various flat rings of the same outside diameter as the top of the bath, and adapted to receive dishes and crucibles of different sizes, are essential adjuncts to the bath. These rings when required are simply laid on the bath.

It will occasionally happen that the water in the bath completely evaporates; in such cases, residues are heated to a higher degree than is desirable, concentrated solutions spirt, &c. To avoid these inconveniences, a water-bath with constant level is employed. Such a bath is shown in fig. , p. , where the reader will find its description.

If the operator can conduct his processes of evaporation in a room set apart for the purpose, where he may easily guard against any occurrence tending to suspend dust in the air, he will find it no very difficult task to keep the evaporating fluid clean; in this case it is best to leave the dishes uncovered. But in a large laboratory, frequented by many people, or in a room exposed to draughts of air, or in which coal fires are burning, the greatest caution is required to protect the evaporating fluid from contamination by dust or ashes.

For this purpose the evaporating dish is either covered with a sheet of filtering-paper turned down over the edges, or a glass rod twisted into a triangular shape (fig. 28) is laid upon it, and a sheet of filtering-paper spread over it, which is kept in position by a glass rod laid across, the latter again being kept from rolling down by the slightly turned up ends, *a* and *b*, of the triangle.

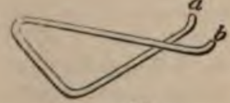

Fig. 28.

The best way, however, is the following:—Take two small thin wooden hoops (fig. 29), one of which fits loosely in the other; spread a sheet of blotting-paper over the smaller one, and push the other over it. This forms a cover admirably adapted to the purpose; and whilst in no way interfering with the operation, it completely protects the evaporating fluid from dust, and may be readily taken off; the paper cannot dip into the fluid; the cover lasts a long time, and may, moreover, at any time be easily renewed.

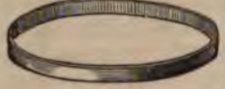

Fig. 29.

It must be borne in mind, however, that the common filtering-paper contains always certain substances soluble in acids, such as lime, sesquioxide of iron, &c., which, were covers of the kind just described used over evaporating dishes containing a fluid evolving acid vapors, would infallibly dissolve in these vapors, and the solution dripping down into the evaporating fluid, would speedily contaminate it. Care must be taken, therefore, in such cases, to use only such filtering-paper as has been freed by washing from substances soluble in acids.

Evaporation for the purpose of concentration may be effected also in flasks; these are only half filled, and placed in a slanting position. The process may be conducted on the sand-bath, or over a gas- or spirit-lamp, or even, and with equal propriety, over a charcoal fire. In cases where the operation is conducted over a lamp or a charcoal fire, it is the safest way to place the flasks on wire gauze. Gentle ebullition of the fluid can do no harm here, since the slanting position of the flask guards effectively against risk of loss from the spirting of the liquid. Still better than in flasks, the object may be attained by evaporating in tubulated retorts with open tubulure and neck directed obliquely upwards. The latter acts as a chimney, and the constant change of air thus effected is extremely favorable to evaporation.

The evaporation of *fluids containing a precipitate* is best conducted on the water-bath; since on the sand-bath, or over the lamp, it is next to impossible to guard against loss from bumping. This bumping is occasioned by slight explosions of steam, arising from the sediment impeding the uniform diffusion of the heat. Still there remains another, though less safe way, viz., to conduct the evaporation in a crucible placed in a slanting position, as illustrated in fig. 30. In this process, the flame is made to play upon the crucible above the level of the fluid.

Where a fluid has to be evaporated to dryness, as is so often the case, the operation should always, if possible, be terminated on the water-bath. In cases where the nature of the dissolved substance precludes the application of the water-bath, the object in view may often be most readily attained by heating the contents of the dish from the top, which is effected by placing the dish in a proper position in a drying closet, whose upper plate is heated by a flame (that of the water- or sand-bath) passing over it. If the substance is in a covered platinum dish or crucible, place the gas-lamp in such a position that the flame may act on the cover from above.

In cases where the heat has to be applied from the bottom, a method must be chosen which admits of an equal diffusion and ready regulation of the heat.

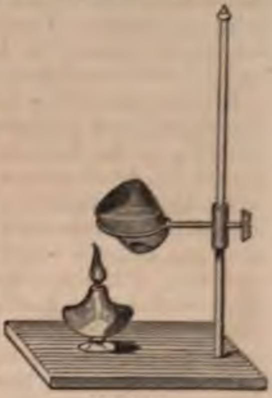
Fig. 30.

An air-bath is well adapted for this purpose, *i.e.*, a dish of iron plate, in which the porcelain or platinum dish is to be placed on a wire triangle, so that the two vessels may be at all points $\frac{1}{4}$ to $\frac{1}{2}$ inch distant from each other. The copper apparatus, fig. 27, may also serve as an air-bath, although I must not omit to mention that this mode of application will in the end seriously injure it. If the operation has to be conducted over a lamp, the dish should be placed high above the flame; best on wire gauze, since this will greatly contribute to an equal diffusion of the heat. The use of the sand-bath is objectionable here, because with that apparatus we cannot reduce the heat so speedily as may be desirable. An iron plate heated by gas may perhaps be used with advantage. But no matter which method be employed, *this* rule applies equally to all of them; that the operator must watch the process, from the moment that the residue begins to thicken, in order to prevent spirting, by reducing the heat, and breaking the pellicles which form on the surface, with a glass rod, or a platinum wire or spatula.

Saline solutions that have a tendency, upon their evaporation, to creep up the sides of the vessel, and may thus finally pass over the brim of the latter, thereby involving the risk of a loss of substance, should be heated from the top, in the way just indicated; since by that means the sides of the vessel will get heated sufficiently to cause the instantaneous evaporation of the ascending liquid, preventing thus its overflowing the brim. The inconvenience just alluded to may, however, be obviated also, in most cases, by covering the brim, and the uppermost part of the inner side of the vessel, with a very thin coat of tallow, thus diminishing the adhesion between the fluid and the vessel.

In the case of liquids evolving gas-bubbles upon evaporating, particular caution is required to guard against loss from spirting. The safest way is to heat such liquids in an obliquely-placed flask, or in a beaker covered with a large watch-glass; the latter is removed as soon as the evolution of gas-bubbles has ceased, and the fluid that may have spirted up against it is carefully rinsed into the glass, by means of a washing-bottle. If the evaporation has to be conducted in a dish, a rather capacious one should be selected, and a very moderate degree of heat applied at first, and until the evolution of gas has nearly ceased.

If a fluid has to be evaporated *with exclusion of air*, the best way is to place the dish under the bell of an air-pump, over a vessel with sulphuric acid, and to exhaust; or a tubulated retort may be used, through whose tubulure hydrogen or carbonic acid is passed by the aid of a tube not quite reaching to the surface of the fluid.

The material of the evaporating vessels may exercise a much greater influence on the results of an analysis than is generally believed. Many rather startling phenomena that are observed in analytical processes may arise simply from a contamination of the evaporated liquid by the material of the vessel; great errors may also spring from the same source.

The importance of this point has induced me to subject it to a searching investigation (see Appendix, Analytical Experiments, 1—4), of which I will here briefly intimate the results.

Distilled water kept boiling for some length of time in glass (flasks of Bohemian glass) dissolves very appreciable traces of that material. This is owing to the formation of soluble silicates; the particles dissolved consist chiefly of potassa, or soda and lime, in combination with silicic acid. A much larger proportion of the glass is dissolved by water containing caustic or carbonated alkali; boiling solution of chloride of ammonium also strongly attacks glass vessels. Boiling dilute acids, with the exception, of course, of hydrofluoric and hydrofluosilicic acids, exercise a less powerful solvent action on glass than pure water. Porcelain (Berlin dishes) is much less affected by water than glass; alkaline liquids also exercise a less powerful solvent action on porcelain than on glass; the quantity dissolved is, however, still notable. Solution of chloride of ammonium acts on porcelain as strongly as on glass; dilute acids, though exercising no very powerful solvent action on porcelain, yet attack that material more strongly than glass. It results from these data, that in analyses pretending to a high degree of accuracy, platinum or platinum-iridium or silver dishes should always be preferred. The former may be used in all cases where no free chlorine, bromine, or iodine is present in the fluid, or can be formed during evaporation. Fluids containing caustic alkalies may safely be evaporated in platinum, but not to the point of fusion of the residue. Silver vessels should never be used to evaporate acid fluids nor liquids containing alkaline sulphides; but they are admirably suited for solutions of caustic and carbonated alkalies, as well as of most neutral salts.

§ 42.

We come now to *weighing the residues remaining upon the evaporation of fluids.* We allude here simply to such as are soluble in water; those which are separated by filtration will be treated of afterwards. Residues are generally weighed in the same vessel in which the evaporation has been completed, for which purpose platinum dishes, from 4 to 8 cm. in diameter, provided with light covers, or large platinum crucibles, are best adapted, since they are lighter than porcelain vessels of the same capacity.

However, in most cases, the amount of liquid to be evaporated is too large for so small a vessel, and its evaporation in portions would occupy too much time. The best way, in cases of this kind, is to concentrate the liquid first in a larger vessel, and to terminate the operation afterwards in the smaller weighing vessel.

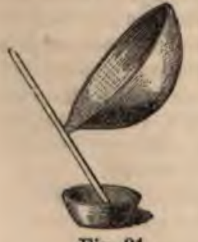
Fig. 31.

In transferring the fluid from the larger to the smaller vessel, the lip of the former is slightly greased, and the liquid made to run down a glass rod. (See fig. 31.)

Finally the large vessel is carefully rinsed with a washing-bottle, until a drop of the last rinsing leaves no longer a residue upon evaporation on a platinum knife. When the fluid has thus been transferred to the weighing-vessel, the evaporation is completed on the water-bath and the residuary substance finally ignited, provided, of course, it will admit of this process. For this purpose the dish is covered with a lid of thin platinum (or a thin glass plate), and then placed high over the flame of a lamp, and heated very gently until all the water which may still adhere to the substance is expelled; the dish is now exposed to a stronger, and finally to a red-heat. (Where a glass plate is used, this must, of course, be removed before igniting.) In this case it is also well to make the flame play obliquely on the cover from above, so as to run as little risk as possible of loss by spirting. After cooling in a desiccator, the covered dish is weighed with its contents. When operating upon substances which decrepitate, such as chloride of sodium, for instance, it is advisable to expose them—after their removal from the water-bath, and previously to the application of a naked flame—to a temperature somewhat above 100°, either in the air-bath, or on a sand-bath, or on a common stove.

If the residue does not admit of ignition, as is the case, for instance, with organic substances, ammoniacal salts, &c., it is dried at a temperature suited to its nature. In many cases, the temperature of the water-bath is sufficiently high for this purpose, for the drying of chloride of ammonium, for instance; in others, the air or oil-bath must be resorted to. (See §§ 29 and 30.) Under any circumstances, the desiccation must be continued until the substance ceases to suffer the slightest diminution in weight, after renewed exposure to heat for half an hour. The dish should invariably be covered during the process of weighing.

If, as will frequently happen, we have to deal with a fluid containing a small quantity of a salt of potassa or soda, the weight of which we want to ascertain, in presence of a comparatively large amount of a salt of ammonia, which has been mixed with it in the course of the analytical process, I prefer the following method: The saline mass is thoroughly dried, in a large dish, on the water-bath, or, towards the end of the process, at a temperature somewhat exceeding 100°. The dry mass is then, with the aid of a platinum spatula, transferred to a small glass dish, which is put aside for a time in a desiccator. The last traces of the salt left adhering to the sides and bottom of the large dish are rinsed off with a little water into the small dish, or the large crucible, in which it is intended to weigh the salt; the water is then evaporated, and the dry contents of the glass dish are added to the residue: the ammonia salts are now expelled by ignition, and the residuary fixed salts finally weighed. Should some traces of the saline mass adhere to the smaller glass dish, they ought to be removed and transferred to the weighing vessel, with the aid of a little pounded chloride of ammonium, or some other salt of ammonia, as the moistening again with water would involve an almost certain loss of substance.

§ 43.

b. PRECIPITATION.

Precipitation is resorted to in quantitative analysis far more frequently than evaporation, since it serves not merely to convert substances into forms adapted for weighing, but also, and more especially, to separate them from one another. The principal intention in precipitation, for the purpose of quantitative estimations, is to convert the substance in solution into a form in which it is insoluble in the menstruum present. The result will, therefore, *cæteris paribus*, be the more accurate, the more the precipitated body deserves the epithet insoluble, and in cases where precipitates are of the same degree of solubility, that one will suffer the least loss which comes in contact with the smallest amount of solvent.

Hence it follows, first, that in all cases where other circumstances do not interfere, it is preferable to precipitate substances in their most insoluble form; thus, for instance, baryta had better be precipitated as sulphate than as carbonate; secondly, that when we have to deal with precipitates that are not quite insoluble in the menstruum present, we must endeavor to remove that menstruum, as far as practicable, by evaporation; thus a dilute solution of strontia should be concentrated, before proceeding to precipitate the strontia with sulphuric acid; and, thirdly, that when we have to deal with precipitates slightly soluble in the liquid present, but insoluble in another menstruum, into which the former may be converted by the addition of some substance or other, we ought to endeavor to bring about this modification of the menstruum. Thus, for instance, alcohol may be added to water, to induce complete precipitation of chloride of platinum and ammonium, chloride of lead, sulphate of lime, &c.; thus again, the basic phosphate of magnesia and ammonia may be rendered insoluble in an aqueous menstruum by adding ammonia to the latter, &c.

Precipitation is generally effected in beakers. In cases, however, where we have to precipitate from fluids in a state of ebullition, or where the precipitate requires to be kept boiling for some time with the fluid, flasks or dishes are substituted for beakers, with due regard always to the material of which they are made (see Evaporation, § 41, at the end).

The separation of precipitates from the fluid in which they are suspended, is effected either by *decantation* or *filtration*, or by both these processes jointly. But, before proceeding to the separation of the precipitate by any of these methods, the operator must know whether the precipitant has been added in sufficient quantity, and whether the precipitate is completely formed. To determine the latter point, an accurate knowledge of the properties of the various precipitates must be attained, which we shall endeavor to supply in the third section. To decide the former question, it is usually sufficient to add to the fluid (after the precipitate has settled) cautiously a fresh portion of the precipitant, and to note if a further turbidity ensues. This test, however, is not infallible, when the precipitate has not the property of forming immediately; as, for instance, is the case with phospho-molybdate of ammonia. When this is apprehended, pour out (or transfer with a pipette) a small quantity of the clear supernatant fluid into another vessel, add some of the precipitant, warm, if necessary; and after some time look and see whether a fresh precipitate has formed. As a general rule, the precipitated liquid should be allowed to stand at rest for several hours, before proceeding to the separation of the precipitate. This rule applies more particularly to crystalline, pulverulent, and gelatinous precipitates, whilst curdy and flocculent precipitates, more particularly when the precipitation was effected at a boiling temperature, may often be filtered off immediately. However, we must observe here, that all general rules, in this respect, are of limited application.

§ 44.

α. SEPARATION OF PRECIPITATES BY DECANTATION.

When a precipitate subsides so completely and speedily in a fluid that the latter may be decanted off perfectly clear, or drawn off with a syphon, or removed by means of a pipette, and that the washing of the precipitate does not require a very long time, decantation is often resorted to for its separation and washing; this is the case, for instance, with chloride of silver, metallic mercury, &c.

Decantation will always be found a very expeditious and accurate method of separation, if the process be conducted with due care; it is necessary, however, in most cases, to promote the speedy and complete subsidence of the precipitate; and it may be laid down as a general rule, that heating the precipitate with the fluid will produce the desired effect. Nevertheless, there are instances in which the simple application of heat will not suffice; in some cases, as with chloride of silver, for instance, agitation must be resorted to; in other cases, some reagent or other is to be added—hydrochloric acid, for instance, in the precipitation of mercury, &c. We shall have occasion, subsequently, in the fourth section, to discuss this point more fully, when we shall also mention the vessels best adapted for the application of this process to the various precipitates.

After having washed the precipitate repeatedly with fresh quantities of the proper fluid, until there is no trace of a dissolved substance to be detected in the last rinsings, it is placed in a crucible or dish, if not already in a vessel of that description; the fluid still adhering to it is poured off as far as practicable, and the precipitate is then, according to its nature, either simply dried, or heated to redness.

A far larger amount of water being required for washing precipitates by decantation than on filters, the former process can be expected to yield *accurate* results only where the precipitates are *absolutely insoluble*. For the same reason, decantation is not ordinarily resorted to in cases where we have to determine other constituents in the decanted fluid.

The decanted fluid must be allowed to stand at rest from twelve to twenty-four hours, to make quite sure that it contains no particles of the precipitate; if, after the lapse of this time, no precipitate is visible, the fluid may be thrown away; but if a precipitate has subsided, this had better be estimated by itself, and the weight added to the main amount; the precipitate may, in such cases, be separated from the supernatant fluid by decantation, or by filtration.

§ 45.

β. SEPARATION OF PRECIPITATES BY FILTRATION.

This operation is resorted to whenever decantation is impracticable, and, consequently, in the great majority of cases; provided always the precipitate is of a nature to admit of its being completely freed, by mere washing on the filter, from all foreign substances. Where this is not the case, more particularly, therefore, with gelatinous precipitates, hydrate of alumina for instance, a combination of decantation and filtration is resorted to (§ 48).

aa. FILTERING APPARATUS.

Filtration, as a process of quantitative analysis, is almost exclusively effected by means of paper.

Plain circular filters are most generally employed; plaited filters are only occasionally used. Much depends upon the quality of the paper. Good filtering-paper must possess the three following properties:—1. It must completely retain the finest precipitates; 2. It must filter rapidly; and 3. It must be as free as possible from any admixture of inorganic bodies, but more especially from such as are soluble in acid or alkaline fluids.

It is a matter of some difficulty, however, to procure paper fully answering these conditions. The *Swedish filtering paper*, with the watermark J. H. MUNKTELL, is considered the best, and, consequently, fetches the highest price; but even this answers only the first two conditions, being by no means sufficiently pure for very accurate analyses, since it leaves upon incineration about 0·3 per cent. of ash,* and yields to acids perceptible traces of lime, magnesia, and sesquioxide of iron. For exact experiments it is, consequently, necessary first to extract the paper with dilute hydrochloric acid, then to wash the acid completely out with water, and finally to dry the paper. In the case of very fine filtering-paper, the best way to perform this operation is to place the ready-cut filters, several together, in a funnel, exactly the same way as if intended for immediate filtration; they are then moistened with a mixture of one part of ordinary pure hydrochloric acid with two parts of water, which is allowed to act on them for about ten minutes; after this all traces of the acid are carefully removed by washing the filters in the funnel repeatedly with warm water. The funnel being then covered with a piece of paper, turned over the edges, is put in a warm place until the filters are dry. Compare the instruction given in the "Qual. Anal.," Am. Ed., p. 8, on the preparation of washed filters. Filter paper containing lead, and which is consequently blackened by sulphuretted hydrogen, should be rejected.

Ready-cut filters of various sizes should always be kept on hand. Filters are either cut by circular patterns of pasteboard or tin, or, still better, by MOHR's filter-patterns, fig. 32. This little apparatus is made of tin-plate, and consists of two parts. *B* is a quadrant fitting in *A*, whose straight edges are turned up, and which is slightly smaller than *B*. The sheets of filter-paper are first cut up into squares, which are folded in quar-

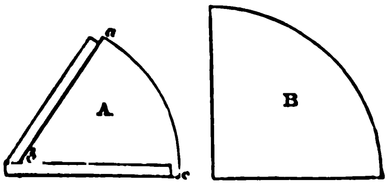

Fig. 32.

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* Plantamour found the ash of Swedish filtering paper to consist of 63·23 silicic acid, 12·83 lime, 0·21 magnesia, 2·94 alumina, and 13·92 sesquioxide of iron, in 100 parts.

ters, and placed in *A*; then *B* is placed on the top, and the free edge of the paper is cut off with scissors. Filters cut in this way are perfectly circular, and of equal size.

Several pairs of these patterns of various sizes (3, 4, 5, 6, 6·5, and 8 cm. radius) should be procured. In taking a filter for a given operation, you should always choose one which, after the fluid has run through, will not be more than half filled with the precipitate.

As to the funnels, they should be inclined at the angle of 60°, and not bulge at the sides. Glass is the most suitable material for them.

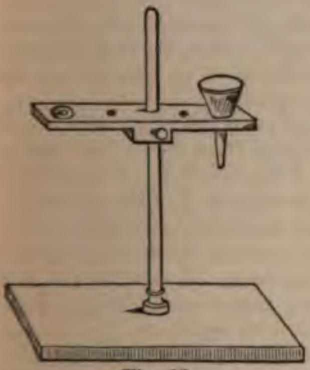

Fig. 33.

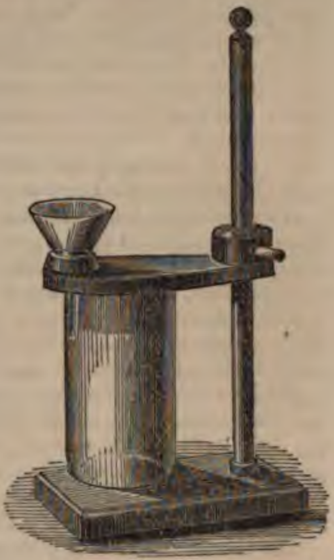

Fig. 34.

The filter should never protrude beyond the funnel. It should come up to one or two lines from the edge of the latter.

The filter is firmly pressed into the funnel, to make the paper fit closely to the side of the latter; it is then moistened with water; any extra water is not poured out, but allowed to drop through.

The stands shown in figs. 33 and 34 complete the apparatus for filtering.

[The stand in fig. 34 serves at once as support for the funnel and cover for the receiving vessel. The funnel is sustained by a ring of wood of such height that only the neck of the funnel comes below the shelf. The shelf is 10 cm., and the ring 15 cm. thick. The opening of the ring above is 30 cm.]

The stands are made of hard wood. The arm holding the funnel or funnels must slide easily up and down, and be fixable by the screw. The holes for the funnels must be cut conically, to keep the funnels steadily in their place.

These stands are very convenient, and may be readily moved about without interfering with the operation.

§ 46.

bb. RULES TO BE OBSERVED IN THE PROCESS OF FILTRATION.

In the case of curdy, flocculent, gelatinous, or crystalline precipitates there is no danger of the fluid passing turbid through the filter. But with fine pulverulent precipitates it is generally *necessary*, and always *advisable*, to let the precipitate subside, and then filter the supernatant liquid, before proceeding to place the precipitate upon the filter. We generally proceed in this way also with other kinds of precipitates, especially with those that require to stand long before they completely separate. Precipitates which have been thrown down hot, are most properly filtered off before cooling (provided always there be no objections to this course), since hot fluids run through the filter more speedily than cold ones. Some precipitates have a tendency to be carried through the filter along with the fluid; this may be prevented in some instances by modifying the latter. Thus sulphate of baryta, when filtered from an aqueous solution, passes rather easily through the filter—the addition of hydrochloric acid or chloride of ammonium prevents this in a great measure.

If the operator finds, during a filtration, that the filter would be much more than half filled by the precipitate, he would better use an additional filter, and thus distribute the precipitate over the two; for, if the first were too full, the precipitate could not be properly washed.

The fluid ought never to be poured directly upon the filter, but always down a glass rod, and the lip or rim of the vessel from which the fluid is poured should always be slightly greased with tallow.* The stream ought invariably to be directed towards the sides of the filter, never to the centre, since this might occasion loss by splashing. In cases where the fluid has to be filtered off, with the least possible disturbance of the precipitate, the glass rod must not be placed, during the intervals, in the vessel containing the precipitate; but it may conveniently be put into a clean glass, which is finally rinsed with the wash-water.

The filtrate is received either in flasks, beakers, or dishes, according to the various purposes for which it may be intended. Strict care should be taken that the drops of fluid filtering through glide down the side of the receiving vessel; they should never be allowed to fall into the centre of the filtrate, since this again might occasion loss by splashing. The best method is that shown in fig. 34, viz., to rest the point of the funnel against the upper part of the inside of the receiving vessel.

If the process of filtration is conducted in a place perfectly free from dust, there is no necessity to cover the funnel, nor the vessel receiving the filtrate; however, as this is but rarely the case, it is generally indispensable to cover both. This is best effected with round plates of sheet-glass. The plate used for covering the receiving vessel should have a small U-shaped piece cut out of its edge, large enough for the funnel-tube to go through. The effect desired may be produced by cautiously chipping out the glass bit by bit with the aid of a key. Plates perforated in the centre are worthless as regards the object in view.

After the fluid and precipitate have been transferred to the filter, and the vessel which originally contained them has been rinsed repeatedly with water, it happens generally that small particles of the precipitate remain adhering to the vessel, which cannot be removed with the glass rod. From beakers or dishes these particles may be readily removed by means of a feather prepared for the purpose by tearing off nearly the whole of the plumules, leaving only a small piece at the end which should be cut perfectly straight. From flasks, minute portions of heavy precipitates which are not adherent, are readily removed by blowing a jet of water into the flask, held inverted over the funnel; this is effected by means of the washing-bottle shown in fig. 36. If the minute adhering particles of a precipitate cannot be removed by mechanical means, solution in an appropriate menstruum must be resorted to, followed by re-precipitation. Bodies for which we possess no solvent, such as sulphate of baryta, for instance, must not be precipitated in flasks.

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* The tallow may be kept under the edge of the work-table at a convenient point, where it will adhere by a little pressure. The best way of applying the tallow to the lip of a vessel is with the greased finger.

§ 47.

cc. WASHING OF PRECIPITATES.

After having transferred the precipitate completely to the filter, we have next to perform the operation of washing; this is effected by means of one of the well-known washing-bottles, of which I prefer the one represented in fig. 35 in every respect. The doubly perforated stoppers are of vulcanized rubber.

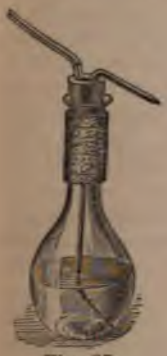
Fig. 35.

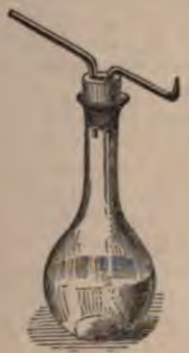
Fig. 36.

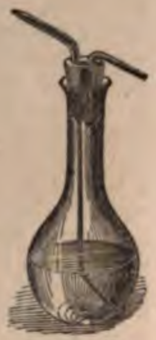
Fig. 37.

Care must always be taken to properly regulate the jet, as too impetuous a stream of water might occasion loss of substance.

In cases where a precipitate has to be washed with great caution, the apparatus illustrated in fig. 37 will be found to answer very well.

The construction of this apparatus requires no explanation. When the flask is inverted, it supplies a fine continuous jet of water.

Precipitates requiring washing with water, are washed most expeditiously with hot water, provided always there be no special reason against its use. The washing-bottle shown in fig. 35 is particularly well adapted for this purpose. The cork which is fastened to the neck of the flask with wire serves to facilitate holding it.

It is a rule in washing precipitates not to add fresh wash-water to the filter till the old has quite run through. In applying the jet of water you have to take care on the one hand that the upper edge of the filter is properly washed, and on the other hand that no canals are formed in the precipitate, through which the fluid runs off, without coming in contact with the whole of the precipitate. If such canals have formed and cannot be broken up by the jet, the precipitate must be stirred cautiously with a small platinum knife or glass rod.

The washing may be considered completed when all soluble matter that is to be removed has been got rid of. The beginner who devotes proper attention to the completion of this operation shuns one of the rocks which he is most likely to encounter. Whether the precipitate has been completely washed may generally be ascertained by slowly evaporating a drop of the last washings upon a platinum knife, and observing if a residue is left. But in cases where the precipitate is not altogether insoluble in water (sulphate of strontia, for instance), recourse must be had to more special tests, which we shall have occasion to point out in the course of the work. The student should never discontinue the washing of a precipitate because he simply *imagines* it is finished—he must be certain.

§ 48.

γ. SEPARATION OF PRECIPITATES BY DECANTATION AND FILTRATION COMBINED.

In the case of precipitates which, from their gelatinous nature, or from the firm adhesion of certain coprecipitated salts, oppose insuperable, or, at all events, considerable obstacles to perfect washing on the filter, the following method is resorted to: Let the precipitate subside as far as practicable, pour the nearly clear supernatant liquid on the filter, stir the precipitate up with the washing fluid (in certain cases, where such a course is indicated, heat to boiling), let it subside again, and repeat this operation until the precipitate is almost thoroughly washed. Transfer it now to the filter, and complete the operation with the washing-bottle (see § 47). This method is highly to be recommended; there are many precipitates that can be thoroughly washed only by its application.

In cases where it is not intended to weigh the precipitate washed by decantation, but to dissolve it again, the operation of washing is entirely completed by decantation, and the precipitate not even transferred to the filter. The re-solution of the bulk of the precipitate being effected in the vessel containing it, the filter is placed over the latter, and the solvent passed through it. Although the termination of the operation of washing may be usually ascertained by testing a sample of the washings for one of the substances originally present in the solution which has to be removed (for hydrochloric acid, for instance, with nitrate of silver), still there are cases in which this mode of proceeding is inapplicable. In such cases, and indeed in processes of washing by decantation generally, BUNSEN's method will be found convenient—viz., to continue the process of washing until the fluid which had remained in the beaker, after the first decantation, has undergone a ten thousand-fold dilution. To effect this, measure with a slip of paper the height from the bottom of this beaker to the surface of the fluid remaining in it, together with the precipitate, after the first decantation; then fill the beaker with water, if possible, boiling, and measure the entire height of the fluid; divide the length of the second column by that of the first. Go through the same process each time you add fresh water, and always multiply the quotient found with the number obtained in the preceding calculation, until you reach 10000.

§ 49.

FURTHER TREATMENT OF PRECIPITATES.

Before proceeding to weigh a precipitate, it still remains to convert it into a form of accurately known composition. This is done either by igniting or by drying. The latter proceeding is more protracted and tedious than the former, and is, moreover, apt to give less accurate results. The process of drying is, therefore, as a general rule, applied only to precipitates which cannot bear exposure to a red heat without undergoing total or partial volatilization; or whose residues left upon ignition have no constant composition; thus, for instance, drying is resorted to in the case of sulphide of mercury, sulphide of arsenic, and other metallic sulphides; and also in the case of cyanide of silver, double chloride of platinum and potassium, &c.

But whenever the nature of the precipitate (*e.g.*, sulphate of baryta, sulphate of lead, and many other compounds) leaves the operator at liberty to choose between drying and heating to redness, the latter process is almost invariably preferred.

§ 50.

aa. Drying of Precipitates.

When a precipitate has been collected, washed, and dried on a filter, minute particles of it adhere so firmly to the paper that it is found impossible to remove them. The weighing of dried precipitates involves, therefore, in all accurate analyses, the drying and weighing of the filter also. To obtain accurate results, it is necessary to dry and weigh the filter before using it; the temperature at which the filter is dried must be the same as that to which it is intended subsequently to expose the precipitate. Another condition is that the filtering-paper must not contain any substance liable to be dissolved by the fluid passing through it.

The drying is conducted either in the water-, air-, or oil-bath, according to the degree of heat required. The weighing is performed in a closed vessel, mostly between two clasped watch-glasses (fig. 20), or in a platinum crucible. When the filter appears dry, it is placed between the warm watch-glasses, or in the warm crucible, allowed to cool under a bell-glass, over sulphuric acid, and weighed. The reopened crucible or watch-glasses, together with the filter, are then again exposed for some time to the required degree of heat, and, after cooling, weighed once more. If the weight does not differ from that found at first, the filter may be considered dry, and we have simply to note the collective weight of the watch-glasses, clasp, and filter, or of the crucible and filter.

After the washing of the precipitate has been concluded and the water allowed to run off as far as possible, the filter with the precipitate is taken off the funnel, folded up, and placed upon blotting-paper, which is then kept for some time in a moderately warm place protected from dust; it is finally put into one of the watch-glasses, or into the uncovered platinum crucible, with which it was first weighed, and exposed to the appropriate degree of heat, either in the water-, air-, or oil-bath. When it is judged that the precipitate is dry, the second watch-glass, or the lid of the crucible is put on (with the clasp pushed over the two in the former case), and the whole, after cooling in the desiccator, is weighed. The filter and the precipitate are then again exposed, in the same way, to the proper drying temperature, allowed to cool, and weighed again, the same process being repeated until the weight remains constant or varies only to the extent of a few deci-milligrammes. By subtracting from the weight found the tare of the crucible or watch-glasses and filter, we obtain the weight of the dry precipitate. [The filter must not be dried too long, as it slowly loses weight, and even becomes brown from decomposition when heated to 100° for days together.]

It happens sometimes that the precipitate nearly fills the filter, or retains a considerable amount of water; or sometimes the paper is so thin that its removal from the funnel cannot well be effected without tearing. In all such cases, the best way is to let the filter and precipitate get nearly dry in the funnel, which may be effected readily by covering the latter with a piece of blotting-paper* to keep out the dust, and placing it, supported on a broken beaker (fig. 38), or some other vessel of the kind, on the steam-apparatus or sand-bath, or stove, or on a heated iron plate. For support to a funnel while drying a hollow frustum of a cone open both ends, made of sheet zinc (fig. 39), is convenient. Two sizes may be used, 10 cm. and 12 cm. high respectively. The lower diameter should be from 7 to 8, the upper from 4 to 6 cm.

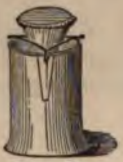
Fig. 38.

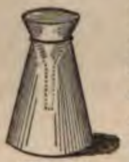
Fig. 39.

§ 51.

bb. Ignition of Precipitates.

In this process it is necessary to burn the filter and subtract the weight of the filter ash from the total weight found.

If care be taken to make the filters always of the same paper, and to cut every size by a pattern, the quantity of ash which each size yields upon incineration may be readily determined. It is necessary, however, to determine separately the quantity of ash left by ordinary filters, and that left by filters which have been washed with hydrochloric acid and water; on an average the latter leave about half as much ash as the former. To determine the filter ash take ten filters (or an equal weight of cuttings from the same paper), burn them in an obliquely-placed platinum crucible, and ignite until every trace of carbon is consumed; then weigh the ash, and divide the amount found by ten; the quotient expresses, with sufficient precision, the average quantity of ash which every individual filter leaves upon incineration.

In the ignition of precipitates, the following four points have to be more particularly regarded:

1. No loss of substance must be incurred;
2. The ignited precipitates must really be the bodies they are represented to be in the calculation of the results;

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* Turned down over the rim. Or more neatly as follows:—Wet a common cut filter, stretch it over the ground top of the funnel, and then gently tear off the superfluous paper. The cover thus formed continues to adhere after drying with some force.

3. The incineration of the filters must be complete;
4. The crucibles must not be attacked.

The following two methods seem to me the simplest and most appropriate of all that have as yet been proposed. The selection of either depends upon certain circumstances, which I shall immediately have occasion to point out. But no matter which method is resorted to, the precipitate must always be thoroughly dried, before it can properly be exposed to a red heat. The application of a red heat to moist precipitates, more particularly to such as are very light and loose in the dry state (silicic acid, for instance), involves always a risk of loss from the impetuously escaping aqueous vapors carrying away with them minute particles of the substance. Some other substances, as hydrate of alumina or hydrated sesquioxide of iron, for instance, form small hard lumps; if such lumps are ignited while still moist within they are liable to fly about with great violence. The best method of drying precipitates as a preliminary to ignition is as described in § 50, the last paragraph.

Respecting the ignition, the *degree* of heat to be applied and the *duration* of the process must, of course, depend upon the nature of the precipitate and upon its deportment at a red heat. As a general rule, a moderate red heat, applied for about five minutes, is found sufficient to effect the purpose; there are, however, many exceptions to this rule which will be indicated wherever they occur.

Whenever the choice is permitted between porcelain and platinum crucibles, the latter are always preferred, on account of their comparative lightness and infrangibility, and because they are more readily heated to redness. The crucible selected should always be of sufficient capacity, as the use of crucibles deficient in size involves the risk of loss of substance. The proper size, in most cases, is 4 cm. in height, and 3·5 cm. in diameter. That the crucible must be perfectly clean, both inside and outside, need hardly be mentioned. The analyst should acquire the habit of cleaning and polishing the platinum crucible always after using it. This should be done by friction with moist sea-sand whose grains are all round and do not scratch. The sand is rubbed on with the finger, and the desired effect is produced in a few minutes. The adoption of this habit is attended with the pleasure of always working with a bright crucible and the profit of prolonging its existence. This mode of cleaning is all the more necessary, when one ignites over gas-lamps, since at this high temperature crucibles soon acquire a gray coating, which arises from a superficial loosening of the platinum. A little burnishing with sea-sand readily removes the appearance in question, without causing any notable diminution of the weight of the crucible. The foregoing remarks on platinum crucibles refer equally to those of iridium-platinum—which, by-the-by, are now much used, and very highly to be recommended—only the restoration of the polish is somewhat more difficult with the latter, on account of the greater hardness of the alloy. If there are spots on the platinum or iridium-platinum crucibles, which cannot be removed by the sand without wearing away too much of the metal, a little bisulphate of potassa is fused in the crucible, the fluid mass shaken about inside, allowed to cool, and the crucible finally boiled with water. There are two ways of cleaning crucibles soiled outside; either the crucible is placed in a larger one, and the interspace filled with bisulphate of potassa, which is then heated to fusion; or the crucible is placed on a platinum-wire triangle, heated to redness, and then sprinkled over with powdered bisulphate of potassa. Instead of the bisulphate you may use borax. Never forget at last to polish the crucible with sea-sand again.

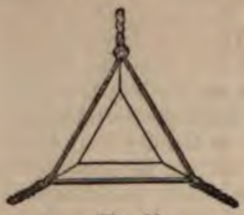

Fig. 40.

When the crucible is clean, it is placed upon a clean platinum-wire triangle (fig. 40), ignited, allowed to cool in the desiccator, and weighed. This operation, though not indispensable, is still always advisable, that the weighing of the empty and the filled crucible may be performed under as nearly as possible the same circumstances. The empty crucible may of course be weighed *after* the ignition of the precipitate; however, it is preferable in most cases to weigh it *before*. The ignition is effected with a BERZELIUS spirit-lamp or a gas-lamp, or else in a muffle. In igniting reducible substances over lamps, the analyst must always be on his guard against the contact of unconsumed hydrocarbons even in covered crucibles. When gas-lamps are used there is especial need of caution in this respect. Reduction will be avoided if the flame is made no larger than necessary, if the crucible is supported in the upper part of the flame, and if, when the crucible is in a slanting position, it is heated from behind.

We pass on now to the description of the special methods.

§ 52.

FIRST METHOD. (*Ignition of the Precipitate with the Filter.*)

This method is resorted to in cases where there is no danger of a reduction of the precipitate by the action of the carbon of the filter. The mode of proceeding is as follows:—

The perfectly dry filter, with the precipitate, is removed from the funnel, and its sides are gathered together at the top, so that the precipitate lies enclosed as in a small bag. The filter is now put into the crucible, which is then covered and heated over a spirit-lamp with double draught, or over gas very gently, to effect the slow charring of the filter; the cover is now removed, the crucible placed obliquely, and a stronger degree of heat applied, until complete incineration of the filter is effected; the lid, which had in the meantime best be kept on a porcelain plate, or in a porcelain crucible, is put on again, and a red heat applied for some time longer, if needed; the crucible is now allowed to cool a little, and is then, while still hot, though no longer red hot,* taken off with a pair of tongs of brass or polished iron (fig. 41), and put in the desiccator, where it is left to cool; it is finally weighed.

The combustion of the carbon of the filter may be promoted, in cases where it proceeds too slowly, by pushing the non-consumed particles, with a smoth and rather stout platinum wire, within the focus of the strongest action of the heat and air. And the operator may also increase the draught of air by leaning the lid of the crucible against the latter in the manner illustrated in fig. 42.

It will occasionally happen that particles of the carbon of the filter obstinately resist incineration. In such cases the operation may be promoted by putting a small lump of fused, dry nitrate of ammonia into the crucible, placing on the lid and applying a gentle heat at first, which is gradually increased. However, as this way of proceeding is apt to involve some loss of substance, its application should not be made a general rule.

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* Taking hold of a *red hot* crucible with brass tongs might cause the formation of black rings round it.

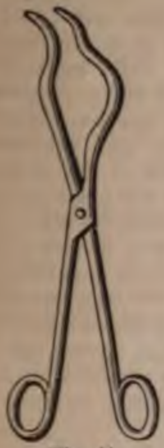
Fig. 41.

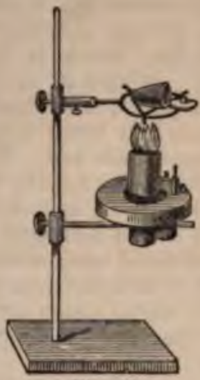
Fig. 42.

In cases where the bulk of the precipitate is easily detached from the filter, the preceding method is occasionally modified in this, that the precipitate is put into the crucible, and the filter, with the still adhering particles, folded loosely together, and laid over the precipitate. In other respects, the operation is conducted in the manner above described.

§ 53.

SECOND METHOD. (*Ignition of the Precipitate apart from the Filter.*)

This method is resorted to in cases where a reduction of the precipitate from the action of the carbon of the filter is apprehended; and also where the ignited precipitate is required for further examination, which the presence of the filter ash might embarrass. It may be employed also, instead of the first method, in all cases where the precipitate is easily detached from the filter. The mode of proceeding is as follows:—

The crucible intended to receive the precipitate is placed upon a sheet of glazed paper; the perfectly dry filter with the precipitate is taken out of the funnel, and gently pressed together over the paper, to detach the precipitate from the filter; the precipitate is now shaken into the crucible, and the particles still adhering to the filter are removed from it, as far as practicable, by further pressing or gentle rubbing together of the folded filter, and are then also transferred to the crucible. The filter is now spread open upon the sheet of glazed paper, and then folded in form of a little square box, enclosed on all sides by the parts turned up;

any minute particles of the precipitate that may have dropped on the glazed paper are brushed into this little box, with the aid of a small feather; the box is closed again, rolled up, and one end of a long platinum wire spirally wound round it. The crucible being placed on or above a porcelain plate, the little roll is lighted, and, during its combustion, held over the crucible, so that the falling particles of the precipitate or filter ash may drop into it, or, at least, into the porcelain plate. In this way, and by occasionally holding the little roll again in or against the flame, the incineration of the filter is readily and safely effected. When the operation is terminated, a slight tap will suffice to drop the ash and the remaining particles of the precipitate into the crucible, which is then covered, and the ignition completed as in § 52. Where it is intended to keep the ash separate from the precipitate, it is made to drop into the lid of the crucible, in which case it is better to ignite the crucible with the principal portion of the precipitate first. This method of incinerating the filter, devised by BUNSEN, is preferable to the method formerly in use, in which the filter, freed, as far as practicable, from the precipitate, was burnt either whole or cut up into little bits on the lid of the crucible, the operation being promoted when necessary by gently pressing the still unconsumed particles with a platinum wire, or platinum spatula, against the red-hot lid. No matter which method of incineration is resorted to, the operation must always be conducted in a spot entirely protected from draughts.

Certain precipitates suffer some essential modification in their properties, in their solubility, for instance, from ignition. In cases where a portion of a substance of the kind is required, after the weighing, for some other purpose with which the effects of a red heat would interfere, the two operations of drying and igniting may be combined in the following way:—The precipitate is collected on a filter dried at 100°; it is then also dried, at 100°, and weighed (§ 50). A portion of the dry precipitate is put into a tared crucible, and its exact weight ascertained; it is then exposed to a red heat, allowed to cool in the usual way, and weighed again; the diminution of weight which it has undergone is calculated on the whole amount of the precipitate.

§ 53, a.

BUNSEN'S METHOD OF RAPID FILTRATION.*

A precipitate is washed either by filtration or by decantation: in the former case the portion of liquid not mechanically retained is allowed to drain from the precipitate; in the latter it is separated by simply pouring it away, the foreign substances contained in the precipitate being then removed by the repeated addition of some washing-fluid, in each successive portion of which the precipitate is, as far as possible, uniformly suspended, this process being continued until the amount of impurity becomes so minute that its presence may be entirely disregarded.

Supposing *v* to represent the volume of the moist precipitate remaining at the bottom of the vessel after the decantation, or upon the filtrate after filtration, V the volume of wash-water employed at each successive decantation, n the number of decantations, and $\frac{1}{a}$ the fraction expressing the proportion of the original amount of impurity still remaining in the precipitate after n decantations, then

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* Ann. der Chem. und Pharm., vol. cxlviii. p. 269; Am. Jour. Sci., xlvii. p. 321.

$$\left(\frac{v}{v+\mathrm{V}}\right)^n=\frac{1}{a}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Calling W the total volume of wash-water resulting from n decantations, then

$$n\mathrm{V}=\mathrm{W}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

therefore

$$\left(1+\frac{\mathrm{W}}{nv}\right)^n=a,$$

or

$$\mathrm{W}=nv\left(\sqrt[n]{a}-1\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If we differentiate W with respect to n and make the differential quotient equal to 0, then the minimum value of W becomes, when $n=\infty$,

$$\mathrm{W}=v \text{ nat. log. } a. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Precipitates obtained in the course of chemical analysis may in all cases be assumed to be sufficiently washed when the impurity retained by them amounts to no more than the $\frac{1}{100000}$ part. Making therefore $a=100000$ and $v=1$, it results from equation (4) that the least quantity of fluid required in order to remove the impurity contained in a precipitate to the $\frac{1}{100000}$ part amounts to eleven and a half times the volume occupied by the precipitate itself in the liquid in which it exists. It is evident, therefore, that the amount of water actually necessary to wash a precipitate the more nearly approaches this minimum the oftener we decant, and the smaller the quantity of washing-water we employ at each decantation.

Since some of the principal sources of error in analytical work consist in the incomplete or in the too protracted washing of precipitates, it becomes important to know how to ascertain the progress of the washing throughout the several stages of the process. By employing the same volume of water at each successive addition, and estimating its relation to that of the precipitate remaining at the bottom of the vessel or upon the filter, we can find from the Table on the following page, calculated by means of the formula above given, the number of times it is necessary to decant in order to diminish the amount of impurity in the precipitate to the $\frac{1}{100000}$, $\frac{1}{50000}$, $\frac{1}{20000}$ or $\frac{1}{10000}$ part. Column I. shows the relation between the volume of the precipitate and the washing-water employed for each successive decantation, column II. the number of decantations required to diminish the amount of impurity to the necessary extent, and column III. the total volume of water obtained from the several decantations.

When the washing-process is performed in a beaker, the relation between the volume of the precipitate and that of the liquid may be easily determined by holding a strip of paper along the side of the vessel and marking upon it the respective heights of the precipitate and supernatant liquid; then on folding the portion of paper lying between the two marks in such a manner that each fold corresponds to the height occupied by the precipitate, the number of folds will give the argument in column I. to find in column II. the number of decantations needed to wash to the required extent. If the washing be conducted as in the ordinary method of filtration, funnels possessing an angle of 60° must be invariably employed, and the capacities of the various-sized filters once for all determined by means of a burette. After the precipitate has been brought upon the filter and allowed to drain, it is mixed as thoroughly as possible with water from a graduated washing-flask. Call the amount of water thus necessary to fill the filter $\mathfrak{v}$, and the capacity of the empty filter $\mathfrak{b}$, then $\frac{\mathfrak{v}}{\mathfrak{b}-\mathfrak{v}} = \frac{V}{v}$ in column I.; that is, the argument needed to find in column II. the number of times it is necessary to refill the filter in order to wash the precipitate to the desired extent.

$\frac{1}{100000}$.			$\frac{1}{50000}$.			$\frac{1}{20000}$.			$\frac{1}{10000}$.		
I.	II.	III.	I.	II.	III.	I.	II.	III.	I.	II.	III.
$\frac{V}{v}$.	n.	W.	$\frac{V}{v}$.	n.	W.	$\frac{V}{v}$.	n.	W.	$\frac{V}{v}$.	n.	W.
0·5	28·4	14·2	0·5	26·7	13·3	0·5	24·4	12·2	0·5	22·7	11·4
1	16·6	16·6	1	15·6	15·6	1	14·3	14·3	1	13·3	13·3
2	10·5	21·0	2	9·8	19·7	2	9·0	18·0	2	8·4	16·8
3	8·3	24·9	3	7·8	23·4	3	7·1	21·4	3	6·6	19·9
4	7·1	28·6	4	6·7	26·9	4	6·1	24·6	4	5·7	22·9
5	6·4	32·1	5	6·0	30·2	5	5·5	27·6	5	5·1	25·7
6	5·9	35·5	6	5·6	33·4	6	5·1	30·5	6	4·7	28·4
7	5·5	38·8	7	5·2	36·4	7	4·8	33·3	7	4·4	31·0
8	5·2	42·0	8	4·9	39·4	8	4·5	36·1	8	4·2	33·5
9	5·0	45·0	9	4·7	42·3	9	4·3	38·7	9	4·0	36·0
10	4·8	48·0	10	4·5	45·1	10	4·1	41·3	10	3·8	38·4
11	4·6	51·0	11	4·4	47·9	11	4·0	43·8	11	3·7	40·8
12	4·5	53·9	12	4·2	50·6	12	3·9	46·3	12	3·6	43·1
13	4·4	56·4	13	4·1	53·3	13	3·8	48·8	13	3·5	45·4
14	4·2	59·4	14	4·0	55·8	14	3·7	51·1	14	3·4	47·5
15	4·2	62·3	15	3·9	58·5	15	3·6	53·6	15	3·3	49·8
16	4·1	65·0	16	3·8	61·1	16	3·5	56·0	16	3·3	53·0
17	4·0	67·8	17	3·7	63·6	17	3·4	58·3	17	3·2	54·2
18	3·9	70·4	18	3·7	66·1	18	3·4	60·5	18	3·1	56·3
19	3·8	74·3	19	3·6	68·6	19	3·3	62·8	19	3·1	58·4

I by far prefer using this Table to employing the method generally followed of ascertaining the completion of the washing-process by evaporating a quantity of the filtrate on platinum-foil, since in the latter case it is only possible to obtain an infallible proof when we have to deal with a precipitate possessing an extremely high degree of insolubility; if the precipitate be soluble to any marked extent, the result is completely illusory.

In the process of filtration as hitherto conducted, the time required is so long and the quantity of wash-water needed so great that some simplification of this continually recurring operation is in the highest degree desirable. The following method, which depends not upon the removal of the impurity by simple attenuation, but upon its displacement by forcing the wash-water through the precipitate, appears to me to combine all the requisite conditions and therefore to satisfy the need.

The rapidity with which a liquid filters depends, *cæteris paribus*, upon the difference which exists between the pressure upon its upper and lower surfaces. Supposing the filter to consist of a solid substance, the pores of which suffer no alteration by pressure or by any other influence, then the volume of liquid filtered in the unit of time is nearly proportional to the difference in pressure: this is clearly shown by the following experiments, made with pure water and a filter consisting of a thin plate of artificial pumice-stone. The thin plate of pumice was hermetically fastened into a funnel consisting of a graduated cylindrical glass vessel, the lower end of which was connected with a large thick flask by means of a tightly fitting caoutchouc cork. The pressure in the flask was then reduced by rarefying the air by means of a method to be described upon another occasion; and for each difference of pressure p, measured by a mercury column, the number of seconds t was observed which a given quantity of water occupied in passing through the filter. The following are the results:—

I.

p. metre.	t. ″	pt.
0·179	91·7	16·4
0·190	81·0	15·4
0·282	52·9	14·9
0·472	33·0	15·6

In the ordinary process of filtration, p on the average amounts to no more than 0·004 to 0·008 metre. The advantage gained, therefore, is easily perceived when we can succeed by some simple, practicable, and easily attainable method in multiplying this difference in pressure one or two hundred times, or, say, to an entire atmosphere, without running any risk of breaking the filter. The solution of this problem is very easy: an ordinary glass funnel has only to be so arranged that the filter can be completely adjusted to its side even to the very apex of the cone. For this purpose a glass funnel is chosen possessing an angle of 60°, or as nearly 60° as possible, the walls of which must be completely free from inequalities of every description; and into it is placed a second funnel made of exceedingly thin platinum-foil, and the sides of which possess exactly the same inclination as those of the glass funnel. An ordinary paper filter is then introduced into this compound funnel in the usual manner; when carefully moistened and so adjusted that no air-bubbles are visible between it and the glass, this filter, when filled with a liquid, will support the pressure of an extra atmosphere without ever breaking.

The platinum funnel is easily made from thin platinum-foil in the following manner:—In the carefully chosen glass funnel is placed a *perfectly accurately fitting* filter made of writing-paper; this is kept in position by dropping a little melted sealing-wax between its upper edge and the glass; the paper is next saturated with oil and filled with liquid plaster of Paris, and before the mixture solidifies a small wooden handle is placed in the centre. After an hour or so the plaster cone with the adhering paper filter can be withdrawn by means of the handle from the funnel, to which it accurately corresponds. The paper on the outside of the cone is again covered with oil, and the whole carefully inserted into liquid plaster of Paris contained in a small crucible 4 or 5 centims. in height. After the mixture has solidified, the cone may be easily withdrawn; the adhering paper filter is then detached, and any small pieces of paper still remaining removed by gently rubbing with the finger. In this manner a solid cone is obtained accurately fitting into a hollow cone, and of which the angle of inclination perfectly corresponds with that of the glass funnel.

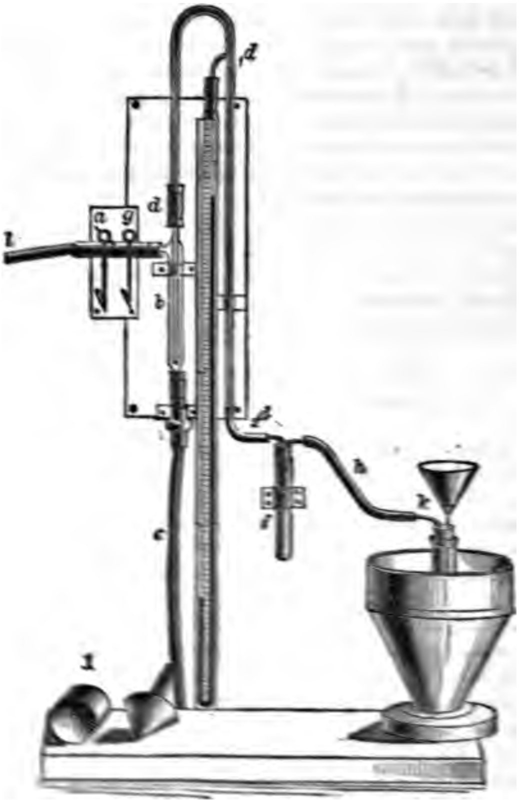

Fig. 43.

Fig. 43, 1, represents the cones. By their help the small platinum funnel is made. A piece of platinum (shown three-fourths of the natural size in fig. 44)* is cut from foil of such a thickness that one square centimetre weighs about 0·154 grm., and from the centre a a vertical incision is made by the scissors to the edge c b d. The small piece of foil is next rendered pliable by being heated to redness, and is placed upon the solid cone in such a manner

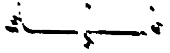

Fig. 44.

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* The diameter of c d in the original drawing is 5·5 centimetres.

that its centre *a* touches the apex of the latter; the sides *a b d* are then closely pressed upon the plaster, and the remaining portion of the platinum wrapped as equally and as closely as possible around the cone. On again heating the foil to redness, pressing it once more upon the cone, and inserting the whole into the hollow cone, and turning it round once or twice under a gentle pressure, the proper shape is completed. The platinum funnel, which should not allow of the transmission of light through its extreme point, even now possesses such stability that it may be immediately employed for any purpose. If desired, it may be made still stronger by soldering down the overlapping portion in one spot only to the upper edge of the foil by means of a grain or two of gold and borax; in general, however, this precaution is unnecessary. If the shape has in any degree altered during this latter process, it is simply necessary to drop the platinum funnel into the hollow cone and then to insert the solid cone, when by one or two turns of the latter the proper form may be immediately restored. The platinum funnel is placed in the bottom of the glass funnel, the dry paper filter then introduced in the ordinary manner, moistened, and freed from all adhering air-bubbles by pressure with the finger. A filter so arranged and in perfect contact with the glass, when filled with a liquid will support the pressure of an entire atmosphere without the least danger of breaking; and the interspace between the folds of the platinum-foil is perfectly sufficient to allow of the passage of a continuous stream of water.

In order to be able to produce the additional pressure of an atmosphere, the filtered liquid is received in a strong glass flask instead of in beakers.* This flask is closed by means of a doubly perforated caoutchouc cork, through one of the holes of which the neck of the glass funnel is passed to a depth of *from* 5 *to* 8 *centimetres* (fig. 43, *k*); through the other is fitted a narrow tube open at both ends, the lower end of which is brought *exactly to the level of the lower surface of the cork*, to the other is adapted the caoutchouc tube connected with the apparatus destined to produce the requisite difference in pressure: this apparatus will be described immediately. The flasks are placed in a metallic or porcelain vessel, in the conical contraction of which several strips of cloth are fastened. This method of supporting the flask has the advantage that, in one and the same vessel, flasks varying in size from 0·5 to 2·5 litres stand equally well, and that by simply laying a cloth over the mouth of the vessel, the consequences of an explosion (which through inexperience or carelessness is possible) are rendered harmless.

It is impossible to employ any of the air-pumps at present in use to create the difference in pressure, since the filtrate not unfrequently contains chlorine, sulphurous acid, hydric sulphide, and other substances which would act injuriously upon the metallic portions of these instruments. I therefore employ a *water* air-pump constructed on the principle of SPRENGEL's mercury-pump, and which appears to me preferable to all other forms of air-pump for chemical purposes, since it effects a rarefaction to within 6 or 12 millimetres pressure of mercury.

Fig. 43 shows the arrangement of this pump. On opening the pinch-cock *a*, water flows from the tube *l* into the enlarged glass vessel *b*, and thence down the leaden pipe *c*. This pipe has a diameter of about 8 millims., and extends downward to a depth of 30 or 40 feet, and ends in a sewer or other arrangement serving to convey the water away. The lower end of the tube *d* possesses a narrow opening; it is hermetically sealed into the wider tube *b*, and reaches nearly to the bottom of the latter. A manometer is attached to the upper continuation of this tube *d* by means of a side tube at d^1; at d^2 is attached a strong thick caoutchouc tube possessing an internal diameter of 5 millims. and an external diameter of 12 millims.; this leads to the flask which is to be rendered vacuous, and is connected with it by means of the short narrowed tube *k*. Between the air-pump and the flask is placed the small thick glass vessel *f*, in which, when one washes with hot water, the steam which may be carried over is condensed. All the caoutchouc joinings are made with very thick tubing, the internal diameter of which amounts to about 5 millims., the external diameter to about 17 millims. The entire arrangement is screwed down upon a board fastened to the wall, in such a manner that each separate piece of the apparatus is held by a single fastening only, in order to prevent the tubes being strained and broken by the possible warping of the board. On releasing the pinchcock *a*, water flows from the conduit *l* down the tube *c* to a depth of more than 30 feet, carrying with it the air which it sucks through the small opening of the tube *d* in the form of a continuous stream of bubbles. No advantage is gained by increasing the rapidity of the flow, since the friction exerted by the water upon the sides of the leaden pipe acts directly as a counter-pressure, and a comparatively small increase in the rapidity of the flow is accompanied by a great increase in the amount of this friction. Accordingly at *g* is a second pinchcock, by which the stream can be once for all so regulated that, on completely opening the cock *a*, the friction, on account of the diminished rate of flow, is rendered sufficiently small to allow of the maximum degree of rarefaction. Such an apparatus, when properly regulated once for all by means of the cock *g*, exhausts in a comparatively short time the largest vessels to within a pressure of mercury equal to the tension of aqueous vapor at the temperature possessed by the stream.* The tension exerted by the water-stream in my laboratory, in which six of these pumps are used, amounts to about 7 millims. in winter and 10 millims. in summer. The filtration is made in the following manner: The flask standing in the metallic or porcelain vessel is connected by means of the slightly drawn-out tube *k* with the caoutchouc tube *h* attached to the pump, the cock *a* having been previously opened and the properly fitted moistened filter filled with the liquid to be filtered. As usual, the clear supernatant fluid is first poured upon the filter; in a moment or two the filtrate runs through in a continuous stream, often so rapidly that one must hasten to keep up the supply of liquid, since it is advisable to maintain the filter as full as possible. After the precipitate has been entirely transferred, the filtrate passes through drop by drop, and the manometer not unfrequently now shows a pressure of an extra atmosphere. The filter may be filled (in fact this is to be recommended) with the precipitate to within a millimetre of its edge, since the precipitate, in consequence of the high pressure to which it is subjected, becomes squeezed into a thin layer broken up by innumerable fissures. As soon as the liquid has passed through and the first traces of this breaking up become evident, the precipitate will be found to have been so firmly pressed upon the paper, that on cautiously pouring water over it it remains completely undisturbed. The washing is effected by carefully pouring water down the side of the funnel to within a centimetre *above* the rim of the filter: the washing flask for this purpose is not applicable; the water must be poured from an open vessel. After the filter has in this manner been replenished four times with water and allowed to drain for a few minutes, it will be found to be already so far dried, in consequence of the high pressure to which it has been subjected, that without any further desiccation it may be withdrawn, together with the precipitate, from the funnel, and immediately ignited, with the precautions to be presently given, in the crucible.

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* These flasks must be somewhat thicker than those ordinarily used, in order to prevent the possibility of their giving way under the atmospheric pressure.

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* The time required to obtain the above degree of exhaustion in a flask of from 1 to 3 litres capacity ranges from six to ten minutes; the quantity of water necessary amounts to about 40 or 50 litres.

If the porosity of a paper filter containing a precipitate were as unalterable as that of a pumice-stone filter, the experiments above described would show that the times required for filtration, according to the old method on the one hand, and the new one on the other, would be inversely proportional to the difference in pressure in each case; that is, by using the pump under the full pressure of about 740 millims., the time needed to wash a precipitate, occupying by the old process an hour, would at the utmost not amount to more than 30 seconds. In using such pumice filters* to drain crystals from adhering mother liquors, or, say, to wash crystals of chromic acid by means of concentrated sulphuric acid and fuming nitric acid, the time occupied in the filtration is scarcely longer than that needed to pour a liquid slowly from one vessel to another. In filtering by means of paper, the precipitate gradually closes up the pores of the filter, and accordingly such an extraordinary acceleration as this can no longer be expected. But the following examples will show the saving of time and labor the method effects, even under all unfavorable conditions. For these experiments I have purposely chosen the hydrated chromium sesquioxide, since it is one of the most difficult of precipitates to wash thoroughly. A solution of chromium chloride was prepared by acting with fuming hydrochloric acid upon potassium dichromate; and by means of a measuring-vessel, which allowed the amount of chromium to be estimated to within 0·0001 grm., successive portions of the liquid were withdrawn, and the chromium oxide contained in them precipitated with the usual precautions by ammonia. The volume of liquid, the quantity of ammonia employed, the time occupied in boiling and in permitting the precipitate to settle, the angle of inclination possessed by the funnel, and the size of the filter were the same in all the experiments. All the precipitates were washed with hot water, and, after burning the filter, ignited over a blast-lamp for a few minutes; in weighing, the platinum crucible was tared by one of about equal weight, and the position of equilibrium of the beam determined by vibrations.

I first attempted to filter one of the precipitates in the ordinary way. $\frac{V}{v}$ amounted to 2; and consequently, from the table, 8·4 fresh additions of water were required in order to wash the precipitate to the $\frac{1}{10000}$ part. The times required were as follows:—

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* Am. Jour. Sci., xlvii. p. 336.

In transferring the precipitate from the beaker and allowing it to drain..................	40′
For the first addition of water to run through,	48
" second " "	70
" third " "	80
Total length of time..................	238

At this point the experiment was discontinued, as the filtrate became turbid. A second experiment failed from the same cause.

Accordingly I attempted to wash the precipitate by decantation. The volume of the precipitate amounted to about 30 cub. centims.; the quantity of water required to fill the beaker was seven times the volume of the precipitate; hence $\frac{V}{v}$ was 7, and the requisite number of decantations to reduce the amount of impurity to the $\frac{1}{10000}$ part was 5·2. The times observed were as follows:—

II.

For the first decantation to run through the filter....	15′
" second " " "	12
" third " " "	18
" fourth " " "	15
" fifth " " "	18
In transferring the precipitate to the filter..........	30
Time required in washing..................	108

Weight of the precipitate..............0·2458 grm.
Volume of wash-water n V............1050 cub. centims.

III.

Experiment repeated. Number of decantations 7. Other circumstances the same as in the foregoing determination.

Time required in washing................ 140′
Weight of the precipitate................ 0·2452 grm.
Volume of wash-water.................. 1200 cub. centims.

IV.

After ten decantations.

Time required in washing.............. 180′
Weight of the precipitate.............. 0·2443 grm.
Volume of wash-water................. 1750 cub. centims.

By filtration with the platinum cone and the pump the following results were obtained:—

V.

In transferring the precipitate to the filter (17 cub. centims. water)..	6′

For the first addition of water (25 cub. cent.) to run through,	2′
" second " " "	3
" third " " "	2
" fourth " " "	2
" fifth " " "	2
In draining the precipitate	2
Time required	19

Weight of precipitate	0·2435 grm.
Volume of wash-water	142 cub. centims.
Pressure of manometer	0·576 metre.

VI.

In transferring the precipitate and allowing the water (18 cub. centims.) to run through	8′
For the first addition of water (25 cub. cent.) to run through	4
" second " " " "	5
" third " " " "	5
" fourth " " " "	5
In draining the precipitate	1
Time required	28

Weight of precipitate	0·2434 grm.
Volume of wash-water	118 cub. centims.
Pressure	0·600 metre.

VII.

In transferring the precipitate and allowing the water (20 cub. centims.) to run through	4′
For the first addition of water (25 cub. cent.) to run through	3
" second " " " "	3
" third " " " "	3
In draining the precipitate	3
Time required	16

Weight of precipitate	0·2432 grm.
Volume of wash-water	95 cub. centims.
Pressure	0·584 metre.

VIII.

In transferring with 25 cub. centims. of water	8′
For the first addition of 25 cub. centims. to run through	5
For the second addition of 25 cub. centims. to run through	5
In draining the precipitate	3
Time required	21

Weight of precipitate	0·2435 grm.
Volume of wash-water	72 cub. centims.
Pressure	0·593 metre.

IX.

In transferring with 15 cub. centims. of water and allowing it to run through	7′
For a single addition to run through	3
In draining the precipitate	2
Time required	12

Weight of precipitate	0·2439 grm.
Volume of wash-water	41 cub. centims.
Pressure	0·572 metre.

X.

In transferring the precipitate with 13 cub. centims. of water	5′
For a single addition of water (26 cub. cent.) to run through	8
In draining the precipitate	1
Time required	14

Weight of precipitate	0·2439 grm.
Volume of wash-water	39 cub. centims.
Pressure	0·530 metre.

In washing, by means of decantation, in the ordinary manner, the amounts of chromium sesquioxide found were as follows:—

	grm.				
II.	0·2458,	after 5	decantations,	washed to the	$\frac{1}{50000}$ part.
III.	0·2452	" 7	"	"	$\frac{1}{200000}$ part.
IV.	0·2443	" 10	"	"	$\frac{1}{100000000}$ part.
	0·2451 mean.				

By the use of the pump:—

	grm.		
V.	0·2433,	after 5	additions of water.
VI.	0·2434	" 4	" "
VII.	0·2432	" 3	" "
VIII.	0·2433	" 2	" "
IX.	0·2439	" 1	addition of water.
X.	0·2439	" 1	" "
	0·2436 mean.		

Hence the probable amount of chromium sesquioxide contained in the solution, according to the experiments with the pump, was 0·2436 grm.: according to the old method of decantation it was somewhat higher, namely 0·2451 grm. This excess of 1·5 milligramme shows that the adhesion of the soluble matters to the precipitate and to the filter is, in consequence of the greater pressure, more easily overcome in the new method than in the customary process. It follows, therefore, that we can obtain a more complete washing by the new method than by the old. The old process of decantation required 116 minutes and 1050 cub. centims. of water to effect a washing to the $\frac{1}{50000}$ part: the new, on the contrary, only 12 to 14 minutes and not more than 39 to 41 cub. centims. of wash water.

§ 53, b.

BUNSEN'S METHOD OF DRYING AND IGNITING PRECIPITATES.

If a precipitate be heated in a platinum crucible immediately after filtration by the older process, a portion will inevitably be projected out of the crucible. Hitherto, therefore, it has been necessary to dry the filter and precipitate before ignition. Now to dry a quantity of hydrated chromium sesquioxide containing 0·2436 grm. Cr^2O^3 in a water-bath at 100° C. requires at least five hours; and, moreover, bringing the dried precipitate into the crucible, burning the filter, and gradually igniting the mass is in the highest degree tedious and troublesome. All this expenditure of time and labor may be saved by employing the new method. By its means a precipitate is as completely dried upon the filter in from 1 to 5 minutes as if it had been exposed from 5 to 8 hours in a drying-chamber; and it can immediately, filter and all, be thrown into a platinum or porcelain crucible and ignited without the slightest fear of its spurting. By operating in the following manner the filter burns quietly without flame or smoke; this phenomenon, although remarkable, easily admits of an explanation. The portion of filter-paper free from precipitate is tightly wrapped round the remainder of the filter in such a manner that the precipitate is enveloped in from four to six folds of clean paper. The whole is then dropped into the platinum or porcelain crucible lying obliquely upon a triangle over the lamp, and pushed down against its sides with the finger. The cover is then supported against the mouth of the crucible in the ordinary way, and the ignition commenced by heating the portion of the crucible in contact with the cover. When the flame has the proper size and position, the filter carbonizes quietly without any appearance of flame or considerable amount of smoke. When the carbonization proceeds too slowly, the flame is moved a little toward the bottom of the crucible. After some time the precipitate appears to be surrounded only by an extremely thin envelope of carbon, possessing exactly the form (of course diminished in size) of the original filter; the flame is then increased, and the crucible maintained at a bright-red heat until the carbon contained in this envelope is consumed. The combustion proceeds so quietly that the resulting ash surrounding the precipitate possesses, even to the smallest fold, the exact form of the original filter. If the ash shows here and there a dark color, it is simply necessary to heat the crucible over a blast-lamp for a few minutes to effect the complete removal of the trace of carbon. This method of burning a filter is extremely convenient and accurate; it is only necessary to give a little attention at first to the slow carbonization of the paper, after which the further progress of the operation may be left to itself.

Gelatinous, finely divided, granular, and crystalline precipitates, such as alumina, calcium oxalate, barium sulphate, silica, magnesium ammonium phosphate, &c., may with equal facility be treated in this manner; so that even in this particular the work, in comparison with the method generally adopted, is considerably shortened and simplified.

§ 53, c.

ADVANTAGES OF BUNSEN'S NEW METHOD.

From the above experiments it appears that the time necessary to filter and dry a quantity of chromium sesquioxyd, hitherto requiring about 7 hours, is reduced by the new method to 13 minutes. This saving of time is, moreover, proportionately greater in the case of precipitates more easily filtered than hydrated chromium sesquioxide. Particularly is this so in separating a finely suspended precipitate from a large volume of water. Under these circumstances the clear fluid runs through the filter in a continuous stream, so rapidly that it is scarcely possible to maintain the supply; the entire operation, in fact, requires scarcely more time than that necessary to pour a liquid from one vessel to another. Filtration, therefore, may be effected as quickly through the smallest as through the largest filter. Moreover, the exceedingly small amount of water required to wash a precipitate completely renders unnecessary the tedious evaporations which by the older method are almost inevitable when the filtrate is needed for a further separation. Thus the introduction of impurities from the action of the liquid upon the dish in the course of evaporation is prevented; and also the loss due to the slight solubility of the greater number of precipitates in the wash-water is reduced to a minimum. Supposing we had to analyze an alkaline chromate in which the quantity of chromic acid is equivalent to 0·2436 grm. chromic sesquioxide, as in the above described experiments, then to determine the proportion of alkali, we should, by using the older method, require the preliminary evaporation of about 1050 cub. centims. of liquid; by the new method the evaporation of 40 cub. centims. only is necessary. Now by employing the water-bath, with constant water-level, it is possible, under favorable circumstances, to evaporate in a porcelain dish 1 cub. centim. of water in 27 seconds. Consequently the evaporation of the filtrate obtained by the older method would occupy about eight hours, whilst by the new 18 minutes only are required. The total length of time needed to filter the chromium sesquioxide, wash and dry the precipitate, and evaporate the filtrate is reduced, therefore, from 14 or 15 hours to about 32 minutes.

Experience has shown that, on the average, three or four analyses can now be made in the time formerly demanded by a single one.

Another and an inestimable advantage springs from the peculiar condition of a precipitate filtered by this method. It not unfrequently happens, even in the hands of experienced manipulators, in consequence of the agitation it is necessary to give to the contents of the filter to effect their complete washing, that the surface of the filter becomes injured and torn so that the precipitate becomes mixed with filaments of paper; this is particularly the case in using hot water. Supposing the precipitate to consist of mixed hydrates of the sesquioxides (for example, iron and alumina), it will be found on redissolving in an acid, that the filaments, like tartaric acid, prevent the complete separation of these substances by subsequent precipitation; thus the alumina will contain iron, and on precipitation by means of ammonium sulphide will be colored black. On the other hand, by employing the new method the precipitate coheres so firmly that the introduction of this source of error is impossible, even by using common gray filter-paper. The most gelatinous precipitates, as hydrated ferric oxide, alumina, &c., adhere to the filter in a thin coherent layer, and may be removed, piece after piece, so completely that the paper remains perfectly clean and white. The advantage thus gained where it is necessary to transfer mixed precipitates to another vessel in order to effect their subsequent separation is evident.

Since the bulk of the moist precipitates, particularly that of the more gelatinous, is so much diminished under the high pressure, the precipitate only occupying one-third to one-sixth of its bulk under ordinary circumstances, a filter of one-third to one-sixth of the size usually employed may be taken, and thus the amount of ash proportionately lessened.

§ 53, d.

BUNSEN'S SIMPLIFIED EXHAUSTING APPARATUS.

It is not necessary to use a pump as powerful as that described, since a fall of 10 or 15 feet is sufficient to filter a precipitate according to the above described method, and so far to dry it that it can be immediately ignited in the crucible. The simple arrangement represented in fig. 45 answers this purpose. It consists of two equal-sized bottles, *a* and *a′*, of from 2 to 4 litres capacity, each of which is provided near the bottom with a small stopcock designed to regulate the flow of water. Suppose *a* filled with water and placed upon a shelf as high above the ground as possible, and *a′* placed empty on the floor, and the two stopcocks connected by means of caoutchouc tubing *c*, then on allowing water to flow down the tube the air in the upper bottle becomes somewhat rarefied; and in order to employ the consequent difference in pressure (amounting to a column of mercury about 0·2 metre in height) for the purpose of filtration, it is only necessary to connect the mouth of the upper bottle with the tube of the filter-flask. When the water has ceased to flow, the position of the bottle is reversed, when the operation recommences. So small a pressure as 0·2 metre suffices to render the filter and its contents so far dry that they may be immediately withdrawn from the funnel and ignited without any other preliminary desiccation. The following experiment, made with a portion of the same solution of chromium used in the former determinations, will serve to show the saving of time effected by this simple arrangement:—

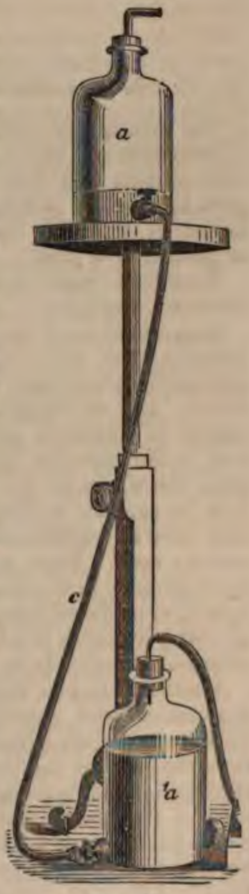

Fig. 45.

XI.

Transferring the precipitate with 14 cub. centims. of water............	14′
For a single addition of 26 cub. centims. of wash-water to run through......	7
To drain the precipitate..............	4
Time required in washing.........	25

Weight of the precipitate	0·2435 grm.
Volume of wash-water	40 cub. centims.
Pressure in manometer	0·184 metre.

This amount of chromium sesquioxide (0·2435 grm.) differs from the mean of the former experiments (0·2436 grm.) by one-tenth of a milligramme only, and shows that even by a pressure of 0·184 metre the washing is as complete by the single addition of 26 cub. centims. of water. The duration of the filtering process in the former experiments ranged from 12 to 14 minutes under a difference of pressure amounting to from 0·53 to 0·572 metre; in the last experiment it required 25 minutes under a pressure of 0·184 metre, or about double the length of time. The time needed to analyze potassium chromate in the former case was reduced from 14 hours to 32 minutes; by the latter method the reduction would be from 14 hours to 44 minutes.

§ 54.

5. Analysis by Measure (Volumetric Analysis).

The principle of volumetric analysis has been explained already in the "Introduction," where we have seen how the quantity of protoxide of iron present in a fluid may be determined by means of a solution of permanganate of potassa, the value of which has been previously ascertained by observing the quantity required to oxidize a known amount of protoxide of iron.

In order to make the matter as clear as possible I will here adduce a few more examples.

Suppose we have prepared a solution of chloride of sodium of such a strength that 100 c. c. will exactly precipitate 1 grm. silver from its solution in nitric acid, we can use it to estimate unknown quantities of silver. Let us imagine, for instance, we have an alloy of silver and copper in unknown proportion, we dissolve 1 grm. in nitric acid, and add to the solution our solution of chloride of sodium, drop by drop, until the whole of the silver is thrown down, and an additional drop fails to produce a further precipitate. The amount of silver present may now be calculated from the amount of solution of chloride of sodium used. Thus, supposing we have used 80 c. c., the amount of silver present in the alloy is 80 per cent.; since, as 100 c. c. of the solution of chloride of sodium will throw down 1 grm. of pure silver (*i.e.* of 100 per cent.), it follows that every c. c. of the chloride of sodium solution corresponds to 1 per cent. of silver.

Another example. It is well known that iodine and sulphuretted hydrogen cannot exist together: whenever these two substances are brought in contact, decomposition immediately ensues, the hydrogen separating from the sulphur and combining with the iodine ($I + HS = HI + S$). Hydriodic acid exercises no action on starch-paste, whereas the least trace of free iodine colors it blue. Now, if we prepare a solution of iodine (in iodide of potassium) containing in 100 c. c. 0·7470 grm. iodine, we may with this decompose exactly 0·1 grm. sulphuretted hydrogen, for 17 : 127 :: 0·1 : 0·7470. Let us suppose, then, we have before us a fluid containing an unknown amount of sulphuretted hydrogen, which it is our intention to determine. We add to it a little starch-paste, and then, drop by drop, our solution of iodine, until a persistent blue coloration of the fluid indicates the formation of iodide of starch, and hence the complete decomposition of the sulphuretted hydrogen. The amount of the latter originally present in the fluid may now be readily calculated from the amount of solution of iodine used. Say, for instance, we have used 50 c. c. of iodine solution, the fluid contained originally 0·05 sulphuretted hydrogen; since, as we have seen, 100 c. c. of our iodine solution will decompose exactly 0·1 grm. of that body.

Solutions of accurately known composition or strength, used for the purposes of volumetric analysis, are called *standard solutions*. They may be prepared in two ways, viz., (*a*) by dissolving a weighed quantity of a substance in a definite volume of fluid; or (*b*), by first preparing a suitably concentrated solution of the reagent required, and then determining its exact strength by a series of experiments made with it upon weighed quantities of the body for the determination of which it is intended to be used.

In the preparation of standard solutions by method *a*, a certain definite strength is adopted once for all, which is usually based upon the principle of an exact correspondence between the number of grammes of the reagent contained in a litre of the fluid, and the equivalent number of the reagent (H=1). In the case of standard solutions prepared by method *b*, this may also be easily done, by diluting to the required degree the still somewhat too concentrated solution, after having accurately determined its strength; however, as a rule, this latter process is only resorted to in technical analyses, where it is desirable to avoid all calculation. Fluids which contain the eq. number of grammes of a substance in one litre, are called *normal solutions;* those which contain $\frac{1}{10}$ of this quantity, *decinormal solutions.*

The determination of a standard solution intended to be used for volumetric analysis is obviously a most important operation; since any error in this will, of course, necessarily falsify every analysis made with it. In scientific and accurate researches it is, therefore, always advisable, whenever practicable, to examine the standard solution—no matter whether prepared by method *a*, or by method *b*, with subsequent dilution to the required degree—by experimenting with it upon accurately weighed quantities of the body for the determination of which it is to be used.

In the previous remarks I have made no difference between fluids of known composition and those of known power; and this has hitherto been usual. But by accepting the two expressions as synonymous, we take for granted that a fluid exercises a chemical action exactly corresponding to the amount of dissolved substance it contains—that, for instance, a solution of chloride of sodium containing 1 eq. Na Cl will precipitate exactly 1 eq. silver. This presumption, however, is very often not absolutely correct, as will be shown with reference to this very example, § 115, *b*, 5. In such cases, of course, it is not merely advisable, but even absolutely necessary, to determine the strength of the fluid by experiment, although the amount of the reagent it contains may be exactly known, for the power of the fluid can be inferred from its composition only approximately and not with perfect exactness. If a standard solution keeps unaltered, this is a great advantage, as it dispenses with the necessity of determining its strength before every fresh analysis.

That particular change in the fluid operated upon by means of a standard solution which marks the completion of the intended decomposition, is termed the FINAL REACTION. This consists either in a *change of color*, as is the case when a solution of permanganate of potassa acts upon an acidified solution of protoxide of iron, or a solution of iodine upon a solution of sulphuretted hydrogen mixed with starch paste; or in the *cessation of the formation of a precipitate* upon further addition of the standard solution, as is the case when a standard solution of chloride of sodium is used to precipitate silver from its solution in nitric acid; or in *incipient precipitation*, as is the case when a standard solution of silver is added to a solution of hydrocyanic acid mixed with an alkali; or in *a change in the action of the examined fluid upon a particular reagent*, as is the case when a solution of arsenite of soda is added, drop by drop, to a solution of chloride of lime, until the mixture no longer imparts a blue tint to paper moistened with iodide of potassium and starch-paste, &c.

The more sensitive a final reaction is, and the more readily, positively, and rapidly it manifests itself, the better is it calculated to serve as the basis of a volumetric method. In cases where it is an object of great importance to ascertain with the greatest practicable precision the exact moment when the reaction is completed, the analyst may sometimes prepare, besides the actual standard solution, another, ten times more dilute, and use the latter to finish the process, carried nearly to completion with the former.

But a good final reaction is not of itself sufficient to afford a safe basis for a good volumetric method; this requires, as the first and most indispensable condition, that the particular decomposition which constitutes the leading point of the analytical process should—at least under certain known circumstances—remain unalterably the same. Wherever this is not the case—where the action varies with the greater or less degree of concentration of the fluid, or according as there may be a little more or less free acid present; or according to the greater or less rapidity of action of the standard solution; or where a precipitate formed in the course of the process has not the same composition throughout the operation—the basis of the volumetric method is fallacious, and the method itself, therefore, of no value.

SECTION II.

REAGENTS.

§ 55.

For general information respecting reagents, I refer the student to my volume on "Qualitative Analysis."

The instructions given here will be confined to the preparation, testing, and most important uses of those chemical substances which subserve principally and more exclusively the purposes of quantitative analysis. Those reagents which are employed in qualitative investigations, having been treated of already in the volume on the qualitative branch of the analytical science, will therefore be simply mentioned here by name.

The reagents used in quantitative analysis are properly arranged under the following heads:—

A. Reagents for gravimetric analysis in the wet way.
B. Reagents for gravimetric analysis in the dry way.
C. Reagents for volumetric analysis.
D. Reagents used in organic analysis.

The mode of preparing the fluids used in volumetric analysis, will be found where we shall have occasion to speak of their application.

A. REAGENTS FOR GRAVIMETRIC ANALYSIS IN THE WET WAY.

I. SIMPLE SOLVENTS.

§ 56.

1. Distilled Water (see "Qual. Anal.").

Water intended for quantitative investigations must be perfectly pure. Water distilled from glass vessels leaves a residue upon evaporation in a platinum vessel (see experiment No. 5), and is therefore inapplicable for many purposes; as, for instance, for the determination of the exact degree of solubility of sparingly soluble substances. For certain uses it is necessary to free the water by ebullition from atmospheric air and carbonic acid.

2. Alcohol (see "Qual. Anal.").

a. Absolute alcohol. *b.* Rectified spirit of wine of various degrees of strength.

3. Ether.

The application of ether as a solvent is very limited. It is more frequently used mixed with spirit of wine, in order to diminish the solvent power of the latter for certain substances, *e.g.*, bichloride of platinum and chloride of ammonium. The ordinary ether of the shops will answer the purpose.

II. ACIDS AND HALOGENS.

a. Oxygen Acids.

§ 57.

1. Sulphuric Acid.

a. Concentrated sulphuric acid of the shops.
b. Concentrated pure sulphuric acid.
c. Dilute sulphuric acid.
See "Qual. Anal."

2. Nitric Acid.

a. Pure nitric acid of 1·2 sp. gr. (see "Qual. Anal.").

b. Red fuming nitric acid (concentrated nitric acid containing some hyponitric acid).

Preparation.—Two parts of pure, dry nitrate of potassa are introduced into a capacious retort, and one part of concentrated sulphuric acid is added either through the tubulure of the retort, or if a common non-tubulated one is used, through the neck by means of a long funnel-tube bent at the lower end, carefully avoiding soiling the neck of the retort. The latter being put into a vessel filled with sand, or, better still, with iron turnings, is then connected with a receiver, but not quite air-tight. The distillation is conducted at a gradually increased heat, and carried to dryness. The cooling of the receiver must be properly attended to during the distillation. In the preparation of small quantities, the retort is placed on a piece of wire-gauze, and heated with charcoal; in this process it is always advisable to coat the retort by repeated application of a thin paste made of clay and water; a little borax or carbonate of soda should be added to the water used for making the paste.

Tests.—Red fuming nitric acid must be in a state of the greatest possible concentration, and perfectly free from sulphuric acid. In order to detect minute traces of the latter, evaporate a few c. c. of the specimen in a porcelain dish nearly to dryness, dilute the residue with water, add some chloride of barium, and observe whether a precipitate forms on standing.

Uses.—A powerful oxidizing agent and solvent; it serves more especially to convert sulphur and metalic sulphides into sulphuric acid and sulphates respectively.

3. Acetic Acid (see "Qual. Anal.").

4. Tartaric Acid (see "Qual. Anal.").

b. Hydrogen Acids and Halogens.

§ 58.

1. Hydrochloric Acid.

a. Pure hydrochloric acid of 1·12 sp. gr. (see "Qual. Anal.").

b. Pure fuming hydrochloric acid of about 1·18 sp. gr.

Preparation.—As in "Qual. Anal." § 26, with this modification, however, that only 3 or 4 parts of water, instead of 6, are put into the receiver, to 4 parts of chloride of sodium in the retort. The greatest care must be taken to keep the receiver cool, and to change it as soon as the tube through which the gas is conducted into it begins to get hot, since it is now no longer hydrochloric acid gas which passes over, but an aqueous solution of the gas, in form of vapor, which would simply weaken the fuming acid, if it were allowed to mix with it.

Tests.—The fuming acid must, for many purposes, be perfectly free from chlorine and sulphurous acid. For the mode of testing for these impurities, see "Qual. Anal." loc. cit. Test for sulphuric acid as under Nitric Acid, previous page.

Uses.—Fuming hydrochloric acid has a much more energetic action than the dilute acid; it is, therefore, used instead of the latter in cases where a more rapid and energetic action is desirable.

2. HYDROFLUORIC ACID.

This is employed for the decomposition of silicates and borates, sometimes in the gaseous form, sometimes in the condition of aqueous solution. In the first case, the substance to be decomposed is introduced into the leaden box, in which the hydrofluoric gas is being generated; in the latter case, we must first prepare the aqueous acid. The raw material employed is fluor spar or kryolite (LUBOLDT*). Both are first finely powdered, and then treated with concentrated sulphuric acid. To 1 part kryolite, 2½ parts sulphuric acid are used; to 1 part fluor spar, 2 parts sulphuric acid are used. If the latter is employed, allow the mixture to stand in a dry place for several days, stirring every now and then, so that the silicic acid (which is generally contained in fluor spar) may first escape in the form of fluosilicic gas. Convenient distillatory apparatus have been described by LUBOLDT (loc. cit.) and by H. BRIEGLEB.† The latter commends itself especially on account of its relatively small cost. It consists of a leaden retort, with a movable leaden top, which can be luted on. The receiver belonging to it is a box of lead, with a tubulure at the side, into which the neck of the retort just enters. The cover of the receiver is raised conical, and is provided at the top with an exit tube of lead. In the receiver a platinum dish containing water is placed, all joints are luted, and the retort is carefully heated in a sand-bath. The aqueous hydrofluoric acid found at the end of the operation in the platinum dish is perfectly pure. The small quantity of impure hydrofluoric acid which collects on the bottom of the receiver is thrown away. The hydrofluoric acid must entirely volatilize when heated in a platinum dish on a water-bath. The pure acid gives no precipitate when neutralized with potash, while silicofluoride of potassium separates if the acid contains hydrofluosilicic acid. The acid is best preserved in gutta-percha bottles, as recommended by STÄDELER. The greatest caution must be observed in preparing this acid, since, whether in the fluid or gaseous condition, it is one of the most injurious substances.

3. CHLORINE AND CHLORINE-WATER (see "Qual. Anal.").

4. NITRO-HYDROCHLORIC ACID (see "Qual. Anal.").

5. HYDROFLUOSILICIC ACID (see "Qual. Anal.").

c. *Sulphur Acids.*

1. HYDROSULPHURIC ACID (see "Qual. Anal.").

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* Journ. für prakt. Chem., 76, 330.

† Annal. d. Chem. u. Pharm., 111, 380.

III. BASES AND METALS.

a. Oxygen Bases and Metals.

§ 59.

α. Alkalies.

1. **Potassa and Soda** (see "Qual. Anal.").

All the three sorts of the caustic alkalies mentioned in the qualitative part are required in quantitative analysis, viz., common solution of soda, hydrate of potassa purified with alcohol, and solution of potassa prepared with baryta. Pure solution of potassa may be obtained also by heating to redness for half an hour in a copper crucible, a mixture of 1 part of nitrate of potassa, and 2 or 3 parts of thin sheet copper cut into small pieces, treating the mass with water, allowing the oxide of copper to subside in a tall vessel, and removing the supernatant clear fluid by means of a syphon (Wöhler).*

2. **Ammonia** (see "Qual. Anal.").

β. Alkaline Earths.

1. **Baryta** (see "Qual. Anal.").

2. **Lime.**

Finely divided hydrate of lime mixed with water (milk of lime), is used more particularly to effect the separation of magnesia, &c., from the alkalies. Milk of lime intended to be used for that purpose must, of course, be perfectly free from alkalies. To insure this the hydrate should be thoroughly washed, by repeated boiling with fresh quantities of distilled water. This operation is conducted best in a silver dish. When cold, the milk of lime so prepared is kept in a well-stoppered bottle.

γ. Heavy Metals, and their Oxides.

§ 60.

1. **Zinc.**

Zinc has of late been much used as a reagent in quantitative analysis. It serves more especially to effect the reduction of dissolved sesquioxide of iron to protoxide, and also the precipitation of copper from the solutions of that metal. Zinc intended to be used for the former purpose must be free from iron, for the latter free from lead, copper, and other metals which remain undissolved upon treating the zinc with dilute acids.

To procure zinc which leaves no residue upon solution in dilute sulphuric acid, there is commonly no other resource but to re-distil the commercial article.

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* Hydrate of soda, made by acting on pure water by pure sodium and fusing in silver vessels, is to be had cheaply of the Magnesium Metal Company, Salford, Manchester, England.

This is effected in a retort made of the material of Hessian or black-lead crucibles. The operation is conducted in a wind-furnace with good draught. The neck of the retort must hang down as perpendicular as possible. Under the neck is placed a basin or small tub, filled with water. The distillation begins as soon as the retort is at a bright red heat. As the neck of the retort is very liable to become choked up with zinc, or oxide of zinc, it is necessary to keep it constantly free by means of a pipe-stem. The zinc obtained by this re-distillation is nearly or quite free from lead.

Tests.—The following is the simplest way of testing the purity of zinc: dissolve the metal in dilute sulphuric acid in a small flask provided with a gas-evolution tube, place the outer limb of the tube under water, and when the solution is completed, let the water entirely or partly recede into the flask; after cooling, add to the fluid, drop by drop, a sufficiently dilute solution of permanganate of potassa. If a drop of that solution imparts the same red tint to the zinc solution as to an equal volume of water, the zinc may be considered free from iron. I prefer this way of testing the purity of zinc to other methods, as it affords, at the same time, an approximate, or, if the zinc has been weighed, and the chameleon solution (which, in that case, must be considerably diluted) measured, an accurate and precise knowledge of the quantity of iron present. If lead or copper are present, these metals remain undissolved upon solution of the zinc.

2. OXIDE OF LEAD.

Precipitate pure nitrate or acetate of lead with carbonate of ammonia, wash the precipitate, dry, and ignite gently to complete decomposition.

Oxide of lead is often used to fix an acid, so that it is not expelled even by a red heat.

b. Sulphur Bases.

1. SULPHIDE OF AMMONIUM (see "Qual. Anal.").

We require both the colorless monosulphide, and the yellow polysulphide.

2. SULPHIDE OF SODIUM (see "Qual. Anal.").

IV. SALTS.

a. Salts of the Alkalies.

§ 61.

1. SULPHATE OF POTASSA (see "Qual. Anal.").

2. OXALATE OF AMMONIA (see "Qual. Anal.").

3. ACETATE OF SODA (see "Qual. Anal.").

4. SUCCINATE OF AMMONIA.

Preparation.—Saturate succinic acid, which has been purified by dissolving in nitric acid and recrystallizing, with dilute ammonia. The reaction of the new compound should be rather slightly alkaline than acid.

Uses.—This reagent serves occasionally to separate sesquioxide of iron from other metallic oxides.

5. Carbonate of Soda (see “Qual. Anal.”).

This reagent is required both in solution and in pure crystals; in the latter form to neutralize an excess of acid in a fluid which it is desirable not to dilute too much.

6. Carbonate of Ammonia (see Qual. Anal.”).

7. Bisulphite of Soda (see “Qual. Anal.”).

8. Hyposulphite of Soda.

This salt occurs in commerce. It should be dry, clear, well crystallized, completely and with ease soluble in water. The solution must give with nitrate of silver at first a white precipitate, must not effervesce with acetic acid, and when acidified must give no precipitate with chloride of barium, or at most, only a slight turbidity. The acidified solution must, after a short time, become milky from separation of sulphur.

Uses.—The hyposulphite of soda is used for the precipitation of several metals, as sulphides, particularly in separations, for instance, of copper from zinc; it also serves as solvent for several salts (chloride of silver, sulphate of lime, &c.); lastly, it is employed in volumetric analysis, its use here depending on the reaction $2\ (NaO,\ S_2\ O_2) + I = Na\ I + Na\ O,\ S_4\ O_5$.

9. Nitrite of Potassa (see “Qual. Anal.”).

10. Bichromate of Potassa (see “Qual. Anal.”).

11. Molybdate of Ammonia (see “Qual. Anal.”).

12. Chloride of Ammonium (see “Qual. Anal.”).

13. Cyanide of Potassium (see “Qual. Anal.”).

b. Salts of the Alkaline Earths.

§ 62.

1. Chloride of Barium (see “Qual. Anal.”).

The following process gives a very pure chloride of barium, free from lime and strontia:—Transmit through a concentrated solution of impure chloride of barium hydrochloric gas, as long as a precipitate continues to form. Nearly the whole of the chloride of barium present is by this means separated from the solution, in form of a crystalline powder. Collect this on a filter, let the adhering liquid drain off, wash the powder repeatedly with small quantities of pure hydrochloric acid, until a sample of the washings, diluted with water, and precipitated with sulphuric acid, gives a filtrate which, upon evaporation in a platinum dish, leaves no residue. The hydrochloric mother-liquor serves to dissolve fresh portions of witherite. I make use of the chloride of barium so obtained, principally for the preparation of perfectly pure carbonate of baryta, which is often required in quantitative analyses.

2. Acetate of Baryta.

Preparation.—Dissolve pure carbonate of baryta in moderately dilute acetic acid, filter, and evaporate to crystallization.

Tests.—Dilute solution of acetate of baryta must not be rendered turbid by solution of nitrate of silver. See also "Qual. Anal.," *Chloride of barium*, the same tests being also used to ascertain the purity of the acetate.

Uses.—Acetate of baryta is used instead of chloride of barium, to effect the precipitation of sulphuric acid, in cases where it is desirable to avoid the introduction of a chloride into the solution, or to convert the base into an acetate. As the reagent is seldom required, it is best kept in crystals.

3. Carbonate of Baryta (see "Qual. Anal.").

4. Chloride of Strontium.

Preparation.—Chloride of strontium is prepared from strontianite or celestine, by the same processes as chloride of barium. The pure crystals obtained are dissolved in spirit of wine of 96 per cent., the solution is filtered, and kept for use.

Uses.—The alcoholic solution of chloride of strontium is used to effect the conversion of alkaline sulphates into chlorides, in cases where it is desirable to avoid the introduction into the fluid of a salt insoluble in spirit of wine.

5. Chloride of Calcium (see "Qual. Anal.").

6. Sulphate of Magnesia (see "Qual. Anal.").

This reagent is principally used to precipitate phosphoric acid from aqueous solutions. The solution required for this purpose should be kept ready prepared; it is made by dissolving 1 part of crystallized sulphate of magnesia and 1 part of pure chloride of ammonium in 8 parts of water and 4 parts of solution of ammonia, allowing the fluid to stand at rest for several days, and then filtering.

This solution is sometimes called magnesia-mixture.

c. *Salts of the Oxides of the Heavy Metals.*

§ 63.

1. Sulphate of Protoxide of Iron (see "Qual. Anal.").

2. Sesquichloride of Iron (see "Qual. Anal.").

3. Acetate of Sesquioxide of Uranium.

Heat finely powdered pitchblende with dilute nitric acid, filter the fluid from the undissolved portion, and treat the filtrate with hydrosulphuric acid to remove the lead, copper, and arsenic; filter again, evaporate to dryness, extract the residue with water, and filter the solution from the oxides of iron, cobalt, and manganese. Nitrate of sesquioxide of uranium crystallizes from the filtrate; purify this by recrystallization, and then heat the crystals until a small portion of the sesquioxide of uranium is reduced. Warm the yellowish-red mass thus obtained with acetic acid, filter and let the filtrate crystallize. The crystals are acetate of sesquioxide of uranium, and the mother-liquor contains the undecomposed nitrate (Wertheim).

Tests.—Solution of acetate of sesquioxide of uranium after acidification with hydrochloric acid must not be altered by hydrosulphuric acid;

carbonate of ammonia must produce in it a precipitate, soluble in an excess of the precipitant.

Uses.—Acetate of sesquioxide of uranium may serve, in many cases, to effect the separation and determination of phosphoric acid.

4. Nitrate of Silver (see "Qual. Anal.").
5. Acetate of Lead (see "Qual. Anal.").
6. Chloride of Mercury (see "Qual. Anal.").
7. Protochloride of Tin (see "Qual. Anal.").
8. Bichloride of Platinum (see "Qual. Anal.").
9. Sodio-Protochloride of Palladium (see "Qual. Anal.").

B. REAGENTS FOR GRAVIMETRIC ANALYSIS IN THE DRY WAY.

§ 64.

1. Carbonate of Soda, pure anhydrous (see "Qual. Anal.").
2. Mixed Carbonates of Soda and Potassa (see "Qual. Anal.").
3. Hydrate of Baryta (see "Qual. Anal." and § 59).
4. Nitrate of Potassa (see "Qual. Anal.").
5. Nitrate of Soda (see "Qual. Anal.").
6. Borax (fused).

Preparation.—Heat crystallized borax (see "Qual. Anal.") in a platinum or porcelain dish, until there is no further intumescence; reduce the porous mass to powder, and heat this in a platinum crucible until it is fused to a transparent mass. Pour the semi-fluid, viscid mass upon a fragment of porcelain. A better way is to fuse the borax in a net of platinum gauze, by making the gas blowpipe-flame act upon it. The drops are collected in a platinum dish. The vitrified borax obtained is kept in a well-stoppered bottle. But as it is always necessary to heat the vitrified borax previous to use, to make quite sure that it is perfectly anhydrous, the best way is to prepare it only when required.

Uses.—Vitrified borax is used to effect the expulsion of carbonic acid and other volatile acids, at a red heat.

7. Bisulphate of Potassa.

Preparation.—Mix 87 parts of neutral sulphate of potassa (see "Qual. Anal."), in a platinum crucible, with 49 parts of concentrated pure sulphuric acid, and heat to gentle redness until the mass is in a state of uniform and limpid fusion. Pour the fused salt on a fragment of porcelain, or into a platinum dish standing in cold water. After cooling, break the mass into pieces, and keep for use.*

Uses.—This reagent serves as a flux for certain native compounds of alumina and sesquioxide of chromium. Bisulphate of potassa is used also, as we have already had occasion to state, for the cleansing of platinum crucibles; for this latter purpose, however, the salt which is obtained in the preparation of nitric acid will be found sufficiently pure.

8. Carbonate of Ammonia (solid).

Preparation.—See "Qual. Anal."—This reagent serves to convert the bisulphates of the alkalies into neutral salts. It must completely volatilize when heated in a platinum dish.

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* [J. Lawrence Smith advises the use of bisulphate of soda for fluxing aluminous compounds, as the fused mass is much more readily soluble in water.]

9. NITRATE OF AMMONIA.

Preparation.—Neutralize pure carbonate of ammonia with pure nitric acid, warm, and add ammonia to slightly alkaline reaction; filter, if necessary, and let the filtrate crystallize. Fuse the crystals in a platinum dish, and pour the fused mass upon a piece of porcelain; break into pieces whilst still warm, and keep in a well-stoppered bottle.

Tests.—Nitrate of ammonia must leave no residue when heated in a platinum dish.

Uses.—Nitrate of ammonia serves as an oxidizing agent; for instance, to convert lead into oxide of lead, or to effect the combustion of carbon, in cases where it is desired to avoid the use of fixed salts.

10. CHLORIDE OF AMMONIUM.

Preparation and Tests.—See "Qual. Anal."

Uses.—Chloride of ammonium is often used to convert metallic oxides and acids, *e.g.*, oxide of lead, oxide of zinc, binoxide of tin, arsenic acid, antimonic acid, &c., into chlorides (ammonia and water escape in the process). Many metallic chlorides being volatile, and others volatilizing in presence of chloride of ammonium fumes, they may be completely removed by igniting them with chloride of ammonium in excess, and thus many compounds, *e.g.*, alkaline antimoniates, may be easily and expeditiously analyzed. Chloride of ammonium is also used to convert various salts with other acids into chlorides, *e.g.*, small quantities of alkaline sulphates.

11. HYDROGEN GAS.

Preparation.—Hydrogen gas is evolved when dilute sulphuric acid is added to granulated zinc. It may be purified from traces of foreign gases either by passing first through chloride of mercury solution, then through potash solution, or as recommended by STENHOUSE, by passing through a tube filled with pieces of charcoal. If the gas is desired dry, pass through sulphuric acid or a chloride of calcium tube.

Tests.—Pure hydrogen gas is inodorous. It ought to burn with a colorless flame, which, when cooled by depressing a porcelain dish upon it, must deposit nothing on the surface of the dish except pure water (free from acid reaction).

Uses.—Hydrogen gas is frequently used, in quantitative analysis, to reduce oxides, chlorides, sulphides, &c., to the metallic state.

12. CHLORINE.

Preparation.—See "Qual Anal."—Chlorine gas is purified and dried by transmitting it through concentrated sulphuric acid, or a chloride of calcium tube.

Uses.—Chlorine gas serves principally to produce chlorides, and to separate the volatile from the non-volatile chlorides; it is also used to displace and indirectly determine bromine and iodine.

C. REAGENTS USED IN VOLUMETRIC ANALYSIS.

§ 65.

Under this head are arranged the most important of those substances, which serve for the preparation and testing of the fluids required in volumetric analysis, and have not been given *sub A* and *B*.

1. PURE CRYSTALLIZED OXALIC ACID.

The introduction of crystallized oxalic acid as a basis for alkalimetry and acidimetry is due to FR. MOHR. It is also employed to determine the strength of, or to *standardize*, a solution of permanganate of potassa, 1 equivalent of permanganic acid being required to convert 5 equivalents of oxalic acid* into carbonic acid ($Mn_2 O_7 + 2 S O_3 + 5 C_2 O_3 = 2 (Mn O, S O_3) + 10 C O_2$). We use in most cases the pure crystallized acid which has the formula $C_2 O_3, H O + 2$ aq., and of which the equivalent is accordingly 63.

Preparation.—Treat powdered oxalic acid of commerce, in a flask, with lukewarm distilled water, in such proportion as will leave a large amount of the acid undissolved, and shake (MOHR). Filter, crystallize, and let the crystals drain; then spread them out on blotting-paper, and let them get thoroughly dry, at the common temperature, in a place free from dust; or press them gently between sheets of blotting-paper, and repeat the operation with fresh sheets, until the crystals are quite dry. Another method, by which the acid is obtained perfectly pure, consists in decomposing oxalate of lead with dilute sulphuric acid.

Tests.—The crystals of oxalic acid must not show the least sign of efflorescence (to which they are liable even at 20° in a dry atmosphere); they must dissolve in water to a perfectly clear fluid; when heated in a platinum dish, they must leave no fixed and incombustible residue (carbonate of lime, carbonate of potassa, &c.). If the acid obtained by a first crystallization fails to satisfy these requirements, it must be recrystallized.

2. TINCTURE OF LITMUS.

Preparation.—Digest 1 part of litmus of commerce with 6 parts of water, on the water-bath, for some time, filter, divide the blue fluid into 2 portions, and saturate in one half the free alkali, by stirring repeatedly with a glass rod dipped in very dilute nitric acid, until the color just appears red; add the remaining blue half, together with 1 part of strong spirit of wine, and keep the tincture, which is now ready for use, in a small open bottle, not quite full, in a place protected from dust. In a stoppered bottle the tincture would speedily loose color.

Tests.—Litmus tincture is tested by coloring with it about 100 cubic centimetres of water distinctly blue, dividing the fluid into two portions, and adding to the one the least quantity of a dilute acid, to the other a trace of solution of soda. If the one portion acquires a distinct red, the other a distinct blue tint, the litmus tincture is fit for use, as neither acid nor alkali predominates.

3. PERMANGANATE OF POTASSA.

Preparation.—Mix 8 parts of very finely powdered pure pyrolusite, or binoxide of manganese, with 7 parts of chlorate of potassa, put the mixture into a shallow cast-iron pot, and add 37 parts of a solution of potassa of 1·27 specific gravity (the same solution as is used in organic analysis†); evaporate to dryness, stirring the mixture during the operation; put the residue before it has absorbed moisture, into an iron or Hessian crucible, and expose to a dull-red heat, with frequent stirring with an iron rod or iron spatula, until no more aqueous vapors escape and the mass is in a faint glow. Remove the crucible now from the fire, and transfer the friable mass to an iron pot. Reduce to coarse powder, and transfer this, in small portions at a time, to an iron vessel containing 100 parts of boiling water; keep boiling, replacing the evaporating water, and passing a stream of carbonic acid through the fluid. (MULDER*). The originally dark green solution of manganate of potassa soon changes, with separation of hydrated binoxide of manganese, to the deep violet-red of the permanganate. When it is considered that the conversion is complete, allow to settle, take out a small quantity of the clear liquid, boil and pass carbonic acid through it. If a precipitate forms, the conversion is not yet complete.

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* Considered as a monobasic acid.

† Or instead of the solution, use 10 parts of the hydrate (K O, H O). In this

The solution may be filtered through gun-cotton. Evaporate, crystallize, and dry the crystals on a porous tile.

The pure salt is now to be obtained in commerce.

4. AMMONIO-SULPHATE OF PROTOXIDE OF IRON.

$$(Fe\ O,\ S\ O_3 + N\ H_4\ O,\ S\ O_3 + 6\ aq.)$$

FR. MOHR has proposed to employ this double salt, which is not liable to efflorescence and oxidation, as an agent to determine the strength of the permanganate solution.

Preparation.—Take two equal portions of dilute sulphuric acid, and warm the one with a moderate excess of small iron nails free from rust, until the evolution of hydrogen gas has altogether or very nearly ceased; neutralize the other portion exactly with carbonate of ammonia, and then add to it a few drops of dilute sulphuric acid. Filter the solution of the sulphate of the protoxide of iron into that of the sulphate of ammonia, evaporate the mixture a little, if necessary, and then allow the salt to crystallize. Let the crystals, which are hard and of a pale green color, drain in a funnel, then wash them in a little water, dry thoroughly on blotting-paper in the air, and keep for use.

The equivalent of the salt (196) is exactly 7 times that of iron (28). The solution of the salt in water which has been just acidified with sulphuric acid must not become red on the addition of sulphocyanide of potassium.

[5. AMMONIA-IRON-ALUM.

$$(Fe_2\ O_3,\ 3\ SO_3 + NH_4\ O,\ SO_3, + 24\ HO.)$$

Preparation.—Bring into a large porcelain dish 58 grms. of pure crystallized ferrous sulphate (see Fresenius' "Qual. Anal." Am. ed. p. 73), together with a quantity of oil of vitriol equivalent to 8·3 grms. of anhydrous sulphuric acid (see Table, p. 488). Heat upon a sand-bath, adding nitric acid from time to time, in small portions, until the iron has all passed into ferric oxide, or until a drop of the solution gives no blue coloration with ferricyanide of potassium. Heat further, and evaporate until the excess of nitric acid is expelled, then add 14 grms.

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case fuse the potash and the chlorate together first, and then project the manganese into the crucible.

[*] Jahresbericht von Kopp und Will, 1858, 581.

of sulphate of ammonia,* and, if need be, hot water sufficient to bring the salt into solution; filter into a porcelain capsule and set aside, under cover, to crystallize.

The iron-alum separates in cubo-octahedrons, which may be yellowish, lilac, or colorless. If dark in color, dissolve in warm water, add a few drops of oil of vitriol, and crystallize again. Rinse the pale or colorless crystals, after separation from the mother-liquor, with cold water, wrap up closely in filter paper, and allow them to dry at the ordinary temperature.†

The yield should be about 80 grms. The dry salt should be pulverized, pressed between folds of paper until freed from mechanically adhering water, and preserved in a well-stoppered bottle.

Uses.—Ammonia-iron-alum furnishes the best means of obtaining a definite quantity of ferric oxide for making standard solutions, being easily obtained pure and inalterable if kept away from acid vapors. Its purity may be readily controlled by ascertaining the loss on careful ignition, which should leave a residue of 16·6 per cent. of sesquioxide of iron, corresponding to 11·59 per cent. of metallic iron.

6. PURE IODINE.

Preparation.—Triturate iodine of commerce with $\frac{1}{4}$ part of its weight of iodide of potassium, dry the mass in a large watch-glass with ground rim, warm this gently on a sand-bath, or on an iron plate, and as soon as violet fumes begin to escape, cover it with another watch-glass of the same size. Continue the application of heat until all the iodine is sublimed, and keep in a well-closed glass bottle. The chlorine or bromine, which is often found in iodine of commerce, combines, in this process, with the potassium, and remains in the lower watch-glass, together with the excess of iodide of potassium.

Tests.—Iodine purified by the process just now described, must leave no fixed residue when heated on a watch-glass. But, even supposing it should leave a trace on the glass, it would be of no great consequence, as the small portion intended for use has to be resublimed immediately before weighing.

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* If not on hand, this salt may be prepared by saturating oil of vitriol with carbonate of ammonia and evaporating to dryness. 30 grammes of oil of vitriol give somewhat more than is required above.

† Examinations of iron-alum thus prepared show that the variations in the color of the salt, from colorless to rose, are not connected with appreciable differences of composition.

J. H. Grove, of the Sheffield Laboratory, obtained the following results in the examination of ammonia-iron-alum crystals, the ferric oxide being estimated by ignition:—

	Fe_2O_3
1st	16·59
	16·53
	16·59
2d	16·53
3d	16·57
4th	16·57
5th	16·58
6th	16·50
	16·56
7th	16·55
Calculated	16·60

Uses.—Pure iodine is used to determine the amount of iodine contained in the solution of iodine in iodide of potassium, employed in many volumetric processes.

7. Iodide of Potassium.

Small quantities of this article may be procured cheaper in commerce than prepared in the laboratory. For the preparation of iodide of potassium intended for analytical purposes I recommend Baup's method, improved by Frederking, because the product obtained by this process is free from iodic acid.

Tests.—Put a sample of the salt in dilute sulphuric acid. If the iodide is pure, it will dissolve without coloring the fluid; but if it contain iodate of potassa, the fluid will acquire a brown tint, from the presence of free iodine ($K\,I + H\,O + S\,O_3 = K\,O, S\,O_3 + H\,I$ and $I\,O_5 + 5\,H\,I = 5\,H\,O + 6\,I$, which remain in solution in the hydriodic acid). Mix the solntion of another sample with nitrate of silver, as long as a precipitate continues to form; add solution of ammonia in excess, shake the mixture, filter, and supersaturate the filtrate with nitric acid. The formation of a white, curdy precipitate indicates the presence of chloride in the iodide of potassium. Presence of sulphate of potassa is detected by means of solution of chloride of barium, with addition of some hydrochloric acid.

Uses.—Iodide of potassium is used as a solvent for iodine in the preparation of standard solutions of iodine; it is employed also to absorb free chlorine. In the latter case every equivalent of chlorine liberates an equivalent of iodine, which is retained in solution by the agency of the excess of iodide of potassium. The iodide of potassium intended for these uses must be free from iodate and carbonate of potassa; the presence of trifling traces of chloride of potassium or sulphate of potassa is of no consequence.

8. Arsenious Acid.

The arsenious acid sold in the shops in large pieces, externally opaque, but often still vitreous within, is generally quite pure. The purity of the article is tested by moderately heating it in a glass tube, open at both ends, through which a feeble current of air is transmitted. Pure arsenious acid must completely volatilize in this process; no residue must be left in the tube upon the expulsion of the sublimate from it. If a non-volatile residue is left which, when heated in a current of hydrogen gas, turns black, the arsenious acid contains teroxide of antimony, and is unfit for use in analytical processes. Dissolve about 10 grms. of the arsenious acid to be tested in soda, and add 1—2 drops acetate of lead. If a brownish color is produced, the arsenious acid contains sulphide of arsenic and cannot be used. Arsenious acid is employed, in form of arsenite of soda, to determine hypochlorous acid, free chlorine, iodine, &c.

9. Chloride of Sodium.

Perfectly pure rock-salt is best suited for analytical purposes. It must dissolve in water to a clear fluid; oxalate of ammonia, phosphate of soda, and chloride of barium must not trouble the solution. Pure chloride of sodium may be prepared also by Margueritte's process, viz., conduct into a concentrated solution of common salt hydrochloric gas to saturation, collect the small crystals of chloride of sodium which separate on a funnel, let them thoroughly drain, wash with hydrochloric acid, and dry the chloride of sodium finally in a porcelain dish, until the hydrochloric acid adhering to it has completely evaporated. The mother-liquor, which contains the small quantities of sulphate of lime, chloride of magnesium, &c., originally present in the salt, is at the next preparation of hydrochloric acid added to the ingredients in the retort, instead of a corresponding portion of water.

Uses.—Chloride of sodium serves as a volumetric precipitating agent in the determination of silver, and also to determine the strength of solutions of silver intended for the estimation of chlorine. We usually fuse it before weighing. The operation must be conducted with caution, and must not be continued longer than necessary; for if the gas-flame acts on the salt, hydrochloric acid escapes, while carbonate of soda is formed.

10. METALLIC SILVER.

The silver obtained by the proper reduction of the pure chloride of the metal alone can be called chemically pure. The silver precipitated by copper is never absolutely pure, but contains generally about $\frac{1}{1000}$ of copper.

Chemically pure silver is only used in small quantity to prepare the dilute solution employed for the determination of silver. The solution of silver required for the estimation of chlorine need not be made with absolutely pure silver, as the strength of this solution had always best be determined *after* the preparation, by means of pure chloride of sodium.

D. REAGENTS USED IN ORGANIC ANALYSIS.

§ 66.

1. OXIDE OF COPPER.

Preparation.—Stir pure* copper scales (which should first be ignited in a muffle) with pure nitric acid in a porcelain dish to a thick paste; after the effervescence has ceased, heat gently on the sand-bath until the mass is perfectly dry. Transfer the green basic salt produced to a Hessian crucible, and heat to a moderate redness, until no more fumes of hyponitric acid escape; this may be known by the smell, or by introducing a small portion of the mass into a test tube, closing the latter with the finger, heating to redness, and then looking through the tube lengthways. The uniform decomposition of the salt in the crucible may be promoted by stirring the mass from time to time with a hot glass rod. When the crucible has cooled a little, reduce the mass, which now consists of pure oxide of copper, to a tolerably fine powder, by triturating it in a brass or porcelain mortar; pass through a metal sieve, and keep in a well-stoppered bottle for use. It is always advisable to leave a small portion of the oxide in the crucible, and to expose this again to an intense red heat. This agglutinated portion is not pounded, but simply broken into small fragments.

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* If the scales contain lime, digest them with water, containing a little nitric acid, for a long time, wash, and then proceed as above.

Tests.—Pure oxide of copper is a compact, heavy, deep-black powder, gritty to the touch; upon exposure to a red heat it must evolve no hyponitric acid fumes, nor carbonic acid; the latter would indicate presence of fragments of charcoal, or particles of dust. It must contain nothing soluble in water. That portion of the oxide which has been exposed to an intense red heat should be hard, and of a grayish-black color.

Uses.—Oxide of copper serves to oxidize the carbon and hydrogen of organic substances, yielding up its oxygen wholly or in part, according to circumstances. That portion of the oxide which has been heated to the most intense redness is particularly useful in the analysis of volatile fluids.

N.B. The oxide of copper, after use, may be regenerated by oxidation with nitric acid, and subsequent ignition. Should it have become mixed with alkaline salts in the course of the analytical process, it is first digested with very dilute cold nitric acid, and washed afterwards with water. To purify oxide of copper containing chloride, E. ERLENMEYER recommends to ignite it in a tube, first in a stream of moist air, and finally, when the escaping gas ceases to redden litmus paper, in dry air. By these operations any oxides of nitrogen that may have remained are also removed.

2. Chromate of Lead.

Preparation.—Precipitate a clear filtered solution of acetate of lead, slightly acidulated with acetic acid, with a small excess of bichromate of potassa; wash the precipitate by decantation, and at last *thoroughly* on a linen strainer; dry, put in a Hessian crucible, and heat to bright redness until the mass is fairly in fusion. Pour out upon a stone slab or iron plate, break, pulverize, pass through a fine metallic sieve, and keep the tolerably fine powder for use.

Tests.—Chromate of lead is a heavy powder, of a dirty yellowish-brown color. It must evolve no carbonic acid upon the application of a red heat; the evolution of carbonic acid would indicate contamination with organic matter, dust, &c. It must contain nothing soluble in water.

Uses.—Chromate of lead serves, the same as oxide of copper, for the combustion of organic substances. It is converted, in the process of combustion, into sesquioxide of chromium and basic chromate of lead. It suffers the same decomposition, with evolution of oxygen, when heated by itself above its point of fusion. The property of chromate of lead to fuse at a red heat renders it preferable to oxide of copper as an oxidizing agent, in cases where we have to act upon difficultly combustible substances.

N.B. Chromate of lead may be used a second time. For this purpose it is fused again (being first roasted, if necessary), and then powdered. After having been twice used it is powdered, moistened with nitric acid, dried, and fused. In this way the chromate of lead may be used over and over again indefinitely (VOHL[*]).

3. Oxygen Gas.

Preparation.—Triturate 100 grammes of chlorate of potassa with exactly 0·1 grm. of finely-powdered sesquioxide of iron, and introduce the mixture into a plain retort, which must not be more than half full; expose the retort, over a charcoal fire, at first to a gentle, and then to a gradually increased heat. As soon as the salt begins to fuse, shake the retort a little, that the contents may be uniformly heated. The evolution of oxygen speedily commences, and proceeds rapidly, but not impetuously, provided the above proportion between the chlorate of potassa and the sesquioxide of iron be adhered to. As soon as the air is expelled from the retort, connect the glass tube, fixed in the neck of the retort by means of a tight-fitting perforated cork, with an india-rubber tube inserted into the lower orifice of the gasometer; the glass tube must be sufficiently wide, and there must be sufficient space left around the india-rubber to permit the free efflux of the displaced water. Continue the application of heat to the retort until, incipient redness having been reached, the evolution of gas has altogether or very nearly ceased. It is advisable to coat the retort up to the middle of the body with several layers of a thin paste made of clay and water, with addition of a little carbonate of soda or borax.

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[*] Annalen d. Chem. u. Pharm., 106, 127.

100 grammes of chlorate of potassa give about 27 litres of oxygen gas.

The oxygen gas produced by this process is moist, and may contain traces of carbonic acid gas, and also of chlorine. The gas prepared from a mixture of chlorate of potassa with a comparatively large proportion of binoxide of manganese always contains a rather considerable quantity of chlorine gas. These impurities must be removed, and the oxygen gas thoroughly dried, before it can be used in elementary organic analysis. The gas is therefore passed from the gasometer, first through a LIEBIG's bulb-apparatus filled with solution of potassa of 1·27 sp. gr., then through a U-tube containing pumice-stone, moistened with sulphuric acid, afterwards through several tubes filled with hydrate of potassa, and lastly through a chloride of calcium tube.

Tests.—A chip of wood which has been kindled and blown out, so as to leave a spark at the extremity, must immediately burst into flame in a current of oxygen gas. The gas must not trouble lime-water, nor solution of nitrate of silver when transmitted through these fluids.

4. SODA-LIME.

Preparation.—Take ordinary solution of soda, ascertain its specific gravity, weigh out a certain quantity, calculate by means of the table, § 206, the weight of the hydrate of soda that must be present, add twice this latter weight of the best quick-lime, and then evaporate to dryness in an iron vessel. Heat the residue in an iron or Hessian crucible, keep for some time at a low red heat, and reduce the mass, whilst still warm, to a tolerably fine powder, by pounding and sifting through a metallic sieve. Keep the powder in a well-stoppered bottle.

Tests.—Soda-lime must not effervesce too much when treated with dilute hydrochloric acid in excess; but, more particularly, it must not evolve ammonia when mixed with pure sugar, and heated to redness. It must not swell and fuse so readily as to obstruct the bore of a tube when heated to low redness, nor must it remain infusible and but loosely coherent after exposure to a bright red-heat. The former difficulty may be remedied by mixture with dry slaked lime, the latter by mixing with a portion of insufficiently ignited soda-lime kept in reserve for this purpose.

Uses.—Soda-lime serves for the analysis of nitrogenous organic substances. For the *rationale* of its action, see the chapter on Organic Analysis.

5. Metallic Copper.

Metallic copper serves, in the analysis of nitrogenous substances, to effect the reduction of the nitric oxide gas that may form in the course of the analytical process.

It is used either in the form of turnings, or in that of close wire spirals; or of small rolls made of thin sheet copper. A length of from 7 to 10 centimetres is given to the spirals or rolls, and just sufficient thickness to admit of their being inserted into the combustion tube. To have it perfectly free from dust, oxide, &c., it is first heated to redness in the open air, in a crucible, until the surface is oxidized; it is then put into a glass or porcelain tube, through which an uninterrupted current of dry hydrogen gas is transmitted; and when all atmospheric air has been expelled from the evolution apparatus and the tube, the latter is in its whole length heated to redness. The operator should make sure that the atmospheric air has been thoroughly expelled, before he proceeds to apply heat to the tube; neglect of this precaution may lead to an explosion.

6. Potassa.

a. Solution of Potassa.

Solution of potassa is prepared from the carbonate, with the aid of milk of lime, in the way described in the "Qualitative Analysis," for the preparation of solution of soda. The proportions are—1 part of carbonate of potassa to 12 parts of water, and $\frac{2}{3}$ part of lime, slaked to paste with three times the quantity of warm water.

The decanted clear solution is evaporated, in an iron vessel, over a strong fire, until it has a specific gravity of 1·27; it is then, whilst still warm, poured into a bottle, which is well closed, and allowed to stand at rest until all solid particles have subsided. The clear solution is finally drawn off from the deposit, and kept for use.

b. Hydrate of Potassa (common).

The commercial hydrate of potassa in sticks will answer the purpose. If you wish to prepare it, evaporate solution of potassa (*a*) in a silver vessel, over a strong fire, until the residuary hydrate flows like oil, and white fumes begin to rise from the surface. Pour the fused mass out on a clean iron plate, and break it up into small pieces. Keep in a well-stoppered bottle for use.

c. Hydrate of Potassa (purified with alcohol), see "Qual. Anal." p. 43.

Uses.—Solution of potassa serves for the absorption, and at the same time for the estimation of carbonic acid. In many cases, a tube filled with hydrate of potassa is used, in addition to the apparatus filled with solution of potassa. Hydrate of potassa purified with alcohol, which is perfectly free from sulphate of potassa, is employed for the determination of sulphur in organic substances.

7. Chloride of Calcium.

a. Crude fused Chloride of Calcium.

Preparation.—Digest, with warm water, the residuary mixture of

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chloride of calcium and lime which remains after the preparation of ammonia; filter, neutralize the alkaline filtrate exactly with hydrochloric acid, and evaporate to dryness in an iron pan; fuse the residue in an iron or Hessian crucible, pour out the fused mass, and break into pieces. Preserve it in well-stoppered bottles.

b. Pure Chloride of Calcium.

Preparation.—Dissolve the crude chloride of calcium of *a* in lime-water, filter the solution, and neutralize exactly with hydrochloric acid; evaporate, in a porcelain dish, to dryness, and expose the residue for several hours to a tolerably strong heat (about 200°), on the sand-bath. The white and porous mass obtained by this process consists of $Ca\,Cl + 2\,aq$.

Uses.—The crude fused chloride of calcium serves to dry moist gases; the pure chloride is used in elementary organic analysis for the absorption and estimation of the water formed by the hydrogen contained in the analyzed substance. The solution of the pure chloride of calcium must not show an alkaline reaction.

8. BICHROMATE OF POTASSA.

Bichromate of potassa of commerce is purified by repeated recrystallization, until chloride of barium produces, in the solution of a sample of it in water, a precipitate which completely dissolves in hydrochloric acid. Bichromate of potassa thus perfectly free from sulphuric acid is required more particularly for the oxidation of organic substances with a view to the estimation of the sulphur contained in them. Where the salt is intended for other purposes, *e.g.*, to determine the carbon of organic bodies, by heating them with chromate of potassa and sulphuric acid, one recrystallization is sufficient.

SECTION III.

FORMS AND COMBINATIONS IN WHICH SUBSTANCES ARE SEPARATED FROM EACH OTHER, OR IN WHICH THEIR WEIGHT IS DETERMINED.

§ 67.

THE quantitative analysis of a compound substance requires, as the first and most indispensable condition, a correct and accurate knowledge of the composition and properties of the new combinations into which it is intended to convert its several individual constituents, for the purpose of separating them from one another, and determining their several weights. Regarding the properties of the new compounds, we have to inquire more particularly, in the first place, how they behave with solvents; secondly, what is their deportment in the air; and, thirdly, what is their behavior on ignition? It may be laid down as a general rule, that compounds are the better adapted for quantitative determination the more insoluble they are, and the less alteration they undergo upon exposure to air or to a high temperature.

The composition of bodies is expressed either in per-cents, or in stoïchiometrical or symbolic formulæ; by means of the latter, the constitution of the more frequently recurring compounds may be easily remembered. In this Section the composition of the substances treated of is given in three different ways, in as many columns: the first column gives the composition of the substance in symbols; the second, in equivalents ($H = 1$); the third, in per-cents. With respect to its composition, a compound is the better adapted for the quantitative determination of a body the less it contains relatively of that body; since any error or loss of substance that may occur in the course of the analytical process will exercise the less influence upon the accuracy of the results. Thus, ammonio-bichloride of platinum, for instance, is, in this respect, better adapted than chloride of ammonium for the determination of nitrogen; since the former contains only 6·27 per cent., while the latter contains 26.2 per cent. of the element in question.

Suppose we have to analyze a nitrogenous substance;—we estimate its nitrogen in the form of bichloride of platinum and chloride of ammonium. When the process is conducted with absolute accuracy, 0·300 grm. of the analyzed body yields 1·000 grm. of ammonio-bichloride of platinum: 100 parts of this double chloride contain 6·27 parts of nitrogen, 1·000 contains therefore 0·0627 of that element. These 0·0627 have been derived from 0·300 of substance; 100 parts of the analyzed body, consequently, contain 20·90 of nitrogen.

We now make a second analysis, in which we convert the nitrogen of the substance to be analyzed into chloride of ammonium, instead of bichloride of platinum and chloride of ammonium: we again conduct the process with absolute accuracy, and obtain from 0·300 of the substance under examination, 0·2394 of chloride of ammonium, corresponding to 0·0627 of nitrogen, or 20·90 per cent.

Now, let us assume a loss of 10 milligrammes to have occurred in each process:—this will alter the result, in the first instance, from 1·000 to 0·990 of bichloride of platinum and chloride of ammonium, corresponding to 0·062073 of nitrogen, or 20·69 per cent.; the loss of nitrogen will therefore be 20·90 − 20·69 = 0·21.

In the second instance the result will be altered from 0·2394 to 0·2294 of chloride of ammonium, corresponding to 0·0601 of nitrogen, or 20.03 per cent. The loss in this case will consequently amount to 0·87.

We see here that the same error occasions, in the one case, a loss of 0·21 per cent., with respect to the amount of nitrogen; whilst, in the other case, the loss amounts to 0·87 per cent.

We will now proceed to enumerate and examine those combinations of the several bodies which are best adapted for their quantitative determination. The description given of the external form and appearance of the new compounds relates more particularly to the state in which they are obtained in our analyses. With regard to the properties of the new compounds, we shall confine ourselves to the enumeration of those which bear upon the special object we have more immediately in view.

A.—FORMS IN WHICH THE BASES ARE WEIGHED OR PRECIPITATED.

BASES OF THE FIRST GROUP.

§ 68.

1. POTASSA (OR POTASH).

The combinations best suited for the weighing of potassa are, SULPHATE OF POTASSA, CHLORIDE OF POTASSIUM, BICHLORIDE OF PLATINUM AND CHLORIDE OF POTASSIUM (Potassio-Bichloride of Platinum).

a. Sulphate of potassa, in the analytical process, is obtained as a white crystalline mass. It dissolves with some difficulty in water (1 part requiring 10 parts of water of 12°), it is almost absolutely insoluble in pure alcohol, but slightly more soluble in alcohol containing sulphuric acid (Expt. No. 6). It does not affect vegetable colors; it is unalterable in the air. The crystals decrepitate strongly when heated. When very strongly ignited for a long time the salt loses weight a little, even when reducing gases are excluded,—the residue possesses an alkaline reaction. When exposed to a red heat, in conjunction with chloride of ammonium, sulphate of potassa is partly, and, upon repeated application of the process wholly, converted, with effervescence, into chloride of potassium (H. Rose).

COMPOSITION.

KO	47·11	54·08
SO_3	40·00	45·92
	87·11	100·00

Bisulphate of potassa ($KO, SO_3 + HO, SO_3$), which is always produced when the neutral salt is evaporated to dryness with free sulphuric acid, is readily soluble in water, and fuses even at a moderate heat. At a red heat [illegible] with the basic water, [illegible] of the acid into the neutral salt requiring the long-continued application of an intense red heat. However, when heated in an atmosphere of carbonate of ammonia—which may be readily procured by repeatedly throwing into the faint red-hot crucible containing the bisulphate, small lumps of pure carbonate of ammonia, and putting on the lid—the acid salt changes readily and quickly to the neutral sulphate. The transformation may be considered complete as soon as the salt, which was so readily fusible before, assumes the solid state, at a faint red heat.

b. Chloride of potassium is obtained in analysis as cubic crystals, or as a crystalline mass. It is readily soluble in water, but much less so in dilute hydrochloric acid; in absolute alcohol it is nearly insoluble, and but slightly soluble in spirit of wine. It does not affect vegetable colors, and is unalterable in the air. When heated it decrepitates, unless it has been kept long drying, with expulsion of a little water mechanically confined in it. At a moderate red heat it fuses unaltered, and without diminution of weight; when exposed to a higher temperature, it volatilizes in white fumes; this volatilization proceeds the more slowly, the more effectually the access of air is prevented (Expt. No. 7). When repeatedly evaporated with solution of oxalic acid in excess, it is converted into oxalate of potassa. When evaporated with excess of nitric acid, it is converted readily and completely into nitrate. On ignition with oxalate of ammonia, carbonate of potassa and cyanide of potassium are formed in noticeable quantities.

K	39·11	52·45
Cl	35·46	47·55
	74·57	100·00

c. Bichloride of platinum and chloride of potassium (Potassio-bichloride of Platinum) presents either small reddish-yellow octahedra, or a lemon-colored powder. It is difficultly soluble in cold, more readily in hot water; nearly insoluble in absolute alcohol, and but sparingly soluble in spirit of wine—one part requiring for its solution, respectively, 12083 parts of absolute alcohol, 3775 parts of spirit of wine of 76 per cent. and 1053 parts of spirit of wine of 55 per cent. (Expt. No. 8, *a*). Presence of free hydrochloric acid sensibly increases the solubility (Expt. No. 8, *b*). In caustic potassa it dissolves completely to a yellow fluid. It is unalterable in the air, and at 100°. On exposure to an intense red heat, 2 eq. of chlorine escape, metallic platinum and chloride of potassium being left; but even after long-continued fusion, there remains always a little potassio-bichloride of platinum which resists decomposition. Complete decomposition is easily effected, by igniting the double salt in a current of hydrogen gas, or with some oxalic acid.

K	39·11	16·00	K Cl	74·57	30·51
Pt	98·94	40·48	Pt Cl_2......	169·86	69·49
Cl_2.......	106·38	43·52			
	244·43	100·00		244·43	100·00

§ 69.

2. SODA.

Soda is usually weighed as SULPHATE OF SODA, CHLORIDE OF SODIUM, or CARBONATE OF SODA. It is separated from potassa in the form of SODIO-BICHLORIDE OF PLATINUM.

a. The anhydrous neutral *sulphate of soda* is a white powder or a white very friable mass. It dissolves readily in water; but is sparingly soluble in absolute alcohol; presence of free sulphuric acid slightly increases its solubility in that menstruum; it is somewhat more readily soluble in spirit of wine (Expt. No. 9). It does not affect vegetable colors; upon exposure to moist air, it slowly absorbs water (Expt. No. 10). When heated to fusion, it scarcely loses weight, but when exposed to a white heat for a long time, it decidedly loses weight, even when reducing gases are excluded; the residue then shows a slight alkaline reaction. When ignited with chloride of ammonium, it comports itself the same as sulphate of potassa under similar circumstances.

$Na\,O$	31	43·66
$S\,O_3$	40	56·34
	71	100·00

Bisulphate of soda ($Na\,O,\,S\,O_3 + H\,O,\,S\,O_3$), which is always produced upon the evaporation of a solution of the neutral salt with sulphuric acid in excess, fuses even at a gentle heat; it may be readily converted into the neutral salt, in the same manner as the bisulphate of potassa is converted into the neutral sulphate (see § 68, *a*).

b. *Chloride of sodium* crystallizes in cubes. In analysis it is frequently obtained as an amorphous mass. It dissolves readily in water, but is much less soluble in hydrochloric acid; it is nearly insoluble in absolute alcohol, and but sparingly soluble in spirit of wine. 100 parts of spirit of wine of 75 per cent. dissolve at a temperature of 15°, 0·7 part. It is neutral to vegetable colors. Exposed to a somewhat moist atmosphere, it slowly absorbs water (Expt. No. 12). Crystals of this salt that have not been kept drying a considerable time decrepitate when heated. The salt fuses at a red heat without decomposition; at a white heat, and in open vessels even at a bright red heat, it volatilizes in white fumes (Expt. No. 13). If a carburetted hydrogen flame acts on fusing chloride of sodium, hydrochloric acid escapes, and some carbonate of soda is formed. On evaporation with oxalic or nitric acids, as well as by ignition with oxalate of ammonia, it comports itself like the corresponding salt of potassa.

Na	23·00	39·34
Cl	35·46	60·66
	58·46	100·00

c. Anhydrous *carbonate of soda* is a white powder or a white very friable mass. It dissolves readily in water, but much less so in solution of ammonia (MARGUERITTE); it is insoluble in alcohol. Its reaction is strongly alkaline. Exposed to the air, it absorbs water slowly. On moderate ignition to incipient fusion it scarcely loses weight; on long fusion, however, it volatilizes to a considerable extent (Comp. Expt. 14).

$Na\,O$	31	58·49
$C\,O_2$	22	41·51
	53	100·00

d. Sodio-bichloride of platinum crystallizes with 6 equivalents of water ($Na\,Cl, Pt\,Cl_2 + 6$ aq.), in light yellow, transparent, prismatic crystals which dissolve readily both in water and in spirit of wine.

§ 70.

3. AMMONIA.

Ammonia is most appropriately weighed as CHLORIDE OF AMMONIUM, or as BICHLORIDE OF PLATINUM AND CHLORIDE OF AMMONIUM (ammonio-bichloride of platinum).

Under certain circumstances, ammonia may also be estimated from the volume of the NITROGEN GAS eliminated from it.

a. Chloride of ammonium is obtained in analysis as a white mass. It dissolves readily in water, but difficultly in spirit of wine. It does not alter vegetable colors, and remains unaltered in the air. Solution of chloride of ammonium, when evaporated on the water-bath, loses a small quantity of ammonia, and becomes slightly acid. The diminution of weight occasioned by this loss of ammonia is very trifling (Expt. No. 15). At 100° chloride of ammonium loses nothing, or very little of its weight (comp. same Expt). At a higher temperature it volatilizes readily, and without undergoing decomposition.

$N\,H_4$	18·00	33·67
Cl	35·46	66·33
	53·46	100·00

$N\,H_3$	17·00	31·80
$H\,Cl$	36·46	68·20
	53·46	100·00

b. Bichloride of platinum and chloride of ammonium (ammonio-bichloride of platinum) occurs either as a heavy lemon-colored powder, or in small, hard octahedral crystals of a bright yellow color. It is difficultly soluble in cold, but more readily in hot water. It is very sparingly soluble in absolute alcohol, but more readily in spirit of wine—1 part requiring of absolute alcohol, 26535 parts; of spirit of wine of 76 per cent., 1406 parts; of spirit of wine of 55 per cent., 665 parts. The presence of free acid sensibly increases its solubility (Expt. No. 16). It remains unaltered in the air, and at 100°. Upon ignition chlorine and chloride of ammonium escape, leaving the metallic platinum as a porous mass (spongy platinum). However, if due care be not taken in this process to apply the heat gradually, the escaping fumes will carry off particles of platinum, which will coat the lid of the crucible.

$N\,H_4$	18·00	8·06
Pt	98·94	44·30
Cl_3	106·38	47·64
	223·32	100·00

NH_3	17·00	7·61
$H\,Cl$	36·46	16·33
$Pt\,Cl_2$	169·86	76·06
	223·32	100·00

$N\,H_4\,Cl$	53·46	23·94
$Pt\,Cl_2$	169·86	76·06
	223·32	100·00

N	14·00	6·27
H_4	4·00	1·79
Pt	98·94	44·30
Cl_3	106·38	47·64
	223·32	100·00

c. Nitrogen gas is colorless, tasteless, and inodorous; it mixes with air without producing the slightest coloration; it does not affect vegetable colors. Its specific gravity is 0·96978 (air = 1). One litre (one cubic decimeter) weighs at 0°, and 0·76 meter of the barometer, 1·25456 grm. It is difficultly soluble in water, 1 volume of water absorbing, at 0°, and 0·76 pressure, 0·02035 vol.; at 10°, 0·01607 vol.; at 15°, 0·01478 vol. of nitrogen gas (BUNSEN).

BASES OF THE SECOND GROUP.

§ 71.

1. BARYTA.

Baryta is weighed as SULPHATE OF BARYTA, CARBONATE OF BARYTA, and SILICO-FLUORIDE OF BARIUM.

a. Artificially prepared *sulphate of baryta* presents the appearance of a fine white powder. When recently precipitated, it is difficult to obtain a clear filtrate, especially if the precipitation was effected without the aid of heat, and the solution contains neither hydrochloric acid nor chloride of ammonium. It is insoluble in cold and in hot water. It has a great tendency, upon precipitation, to carry down with it other substances contained in the solution from which it separates, more particularly nitrate of baryta, chloride of barium, sesquioxide of iron, &c. These substances can generally be completely removed only after ignition, by washing with appropriate solvents. Even the precipitate obtained from a solution of chloride of barium by means of sulphuric acid in excess contains traces of chloride of barium, which it is impossible to remove, even by washing with boiling water, but which are dissolved by nitric acid (SIEGLE). Cold dilute acids dissolve trifling, yet appreciable traces of sulphate of baryta; for instance, 1000 parts of nitric acid of 1·032 sp. gr. dissolve 0·062 parts of $Ba\,O, S\,O_3$. Cold concentrated acids dissolve considerably more; thus, 1000 parts of nitric acid of 1·167 sp. gr. dissolve 2 parts of $Ba\,O, S\,O_3$ (CALVERT). Boiling hydrochloric acid also dissolves appreciable traces; thus 230 c. c. of hydrochloric acid of 1·02 sp. gr. were found, after a quarter of an hour's boiling with 0·679 grm. of sulphate of baryta, to have dissolved of it 0·048 grm. Acetic acid dissolves less sulphate of baryta than the other acids; thus, 80 c. c. of acetic acid of 1·02 sp. gr. were found, after a quarter of an hour's boiling with 0·4 grm. of $Ba\,O, S\,O_3$, to have dissolved only 0·002 grm. (SIEGLE). Free chlorine considerably increases the solubility of sulphate of baryta (O. L. ERDMANN). Several salts more particularly interfere with the precipitation of baryta by sulphuric acid. I observed this some time ago with chloride of magnesium, but nitrate of ammonia (MITTENTZWEY) and alkaline citrates (SPILLER) possess this property in a high degree. In the last case the precipitate appears on the addition of hydrochloric acid. If a fluid contains metaphosphoric acid, baryta cannot be completely precipitated out of it by means of sulphuric acid; the resulting precipitate too is not pure, but contains phosphoric acid (SCHEERER, RUBE). Sulphate of baryta remains quite unaltered in the air at 100°, and even at a red heat. On ignition with charcoal, or under the influence of reducing gases, it is converted comparatively easily, but as a rule only partially, into sulphide of barium. On ignition with chloride of ammonium, sulphate of baryta undergoes partial decomposition. It is not affected, or affected but very slightly, by cold solutions of alkaline bicarbonates or of carbonate of ammonia; solutions of the monocarbonates of the fixed alkalies when cold have only a slight decomposing action upon it; but when boiling, and upon repeated application, they effect at last the complete decomposition of the salt (H. ROSE). By fusion with alkaline carbonates, sulphate of baryta is readily decomposed.

$Ba\,O$	76·5	65·67
SO_3	40·0	34·33
	116·5	100·00

b. Artificially prepared *carbonate of baryta* is a white powder. It dissolves in 14137 parts of cold, and in 15421 parts of boiling water (Expt. No. 17). It dissolves far more readily in solutions of chloride of ammonium or nitrate of ammonia; from these solutions it is, however, precipitated again, though not completely, by caustic ammonia. In water containing free carbonic acid, carbonate of baryta dissolves to bicarbonate. In water containing ammonia and carbonate of ammonia, it is nearly insoluble, one part requiring about 141000 parts (Expt. No. 18). Its solution in water has a very faint alkaline reaction. Alkaline citrates and metaphosphates impede the precipitation of baryta by carbonate of ammonia. It is unalterable in the air, and at a red heat. When exposed to the strongest heat of a blast-furnace, it slowly yields up the whole of its carbonic acid; this expulsion of the carbonic acid is promoted by the simultaneous action of aqueous vapor. Upon heating it to redness with charcoal, caustic baryta is formed, with evolution of carbonic oxide gas.

$Ba\,O$	76·5	77·67
$C\,O_2$	22·0	22·33
	98·5	100·00

c. Silico-fluoride of barium forms small, hard, and colorless crystals, or (more generally) a crystalline powder. It dissolves in 3800 parts of cold water; in hot water it is more readily soluble (Expt. No. 19). The presence of free hydrochloric acid increases its solubility considerably (Expt. No. 20). Chloride of ammonium acts also in the same way (1 part silico-fluoride of barium dissolves in 428 parts of saturated, and 589 parts of dilute solution of chloride of ammonium. J. W. MALLET). In spirit of wine it is almost insoluble. It is unalterable in the air, and at 100°; when ignited, it is decomposed into fluoride of silicon, which escapes, and fluoride of barium, which remains.

$Ba\,Fl$	87·5	62·72	Ba......	68·5	49·10
$Si\,Fl_2$	52·0	37·28	Si	14·0	10·04
			Fl_3	57·0	40·86
	139·5	100·00		139·5	100·00

§ 72.

2. STRONTIA.

Strontia is weighed either as SULPHATE OF STRONTIA, or as CARBONATE OF STRONTIA.

a. Sulphate of strontia, artificially prepared, is a white powder. It dissolves in 6895 parts of cold, and 9638 parts of boiling water (Expt. No. 21). In water containing sulphuric acid, it is still more difficultly soluble, requiring from 11000 to 12000 parts (Expt. No. 22). Of cold hydrochloric acid of 8·5 per cent., it requires 474 parts; of cold nitric acid of 4·8 per cent., 432 parts; of cold acetic acid of 15·6 per cent. of $\bar{A}$, HO, as much as 7843 parts (Expt. No. 23). It dissolves in solution of chloride of sodium, but is precipitated again from this solution by sulphuric acid. Metaphosphoric acid (Scheerer, Rube), and also alkaline citrates, but not free citric acid (Spiller), impede the precipitation of strontia by sulphuric acid. It is nearly insoluble both in absolute alcohol and in spirit of wine. It does not alter vegetable colors; and remains unaltered in the air, and at a red heat. When exposed to a most intense red heat, it fuses without undergoing decomposition. When ignited with charcoal, or under the influence of reducing gases, it is converted into sulphide of strontium. The solutions of carbonates and bicarbonates of potassa, soda, and ammonia decompose sulphate of strontia completely at the common temperature, even when considerable quantities of alkaline sulphates are present (H. Rose). Boiling promotes the decomposition.

$Sr\,O$	51·75	56·40
$S\,O_3$..........	40·00	43·60
	91·75	100·00

b. Carbonate of strontia, artificially prepared, is a white, light, loose powder. It dissolves, at the common temperature, in 18045 parts of water (Expt. No. 24). Presence of ammonia diminishes its solubility (Expt. No. 25). It dissolves pretty readily in solutions of chloride of ammonium and of nitrate of ammonia, but is precipitated again from these solutions by ammonia and carbonate of ammonia, and more completely than carbonate of baryta under similar circumstances. Water impregnated with carbonic acid dissolves it as bicarbonate. Its reaction is very feebly alkaline. Alkaline citrates and metaphosphates impede the precipitation of strontia by alkaline carbonates. Ignited with access of air it is infusible, but when exposed to a most intense heat, it fuses, and gradually loses its carbonic acid. On ignition with charcoal, caustic strontia is formed, with evolution of carbonic oxide gas.

$Sr\,O$..........	51·75	70·17
$C\,O_2$..........	22·00	29·83
	73·75	100·00

§ 73.

3. Lime.

Lime is weighed either as SULPHATE OF LIME, or as CARBONATE OF LIME; to convert it into the latter form, it is first usually precipitated as oxalate of lime.

a. Artificially prepared anhydrous *sulphate of lime* is a loose, white power. It dissolves, at the common temperature, in 430 parts, at 100°, in 460 parts of water (Poggiale). Presence of hydrochloric acid, nitric acid, chloride of ammonium, sulphate of soda, and chloride of sodium, increases its solubility. It dissolves with comparative ease, especially on gently warming, in aqueous solution of hyposulphite of soda (DIEHL). The aqueous solution of sulphate of lime does not alter vegetable colors. In alcohol and in spirit of wine of 90 per cent. it is almost absolutely insoluble. Exposed to the air, it slowly absorbs water. It remains unaltered at a dull red heat. Heated to intense bright redness, it fuses without undergoing decomposition. At a white heat it loses sulphuric acid and its weight is considerably diminished—the residue has an alkaline reaction (AL. MITSCHERLICH *). On ignition with charcoal or under the influence of reducing gases it is converted into sulphide of calcium. Solutions of alkaline carbonates and bicarbonates decompose sulphate of lime more readily still than sulphate of strontia.

CaO	28	41·18
SO_3	40	58·82
	68	100·00

b. Artificially prepared *carbonate of lime* is a fine white powder. It dissolves in 10601 parts of cold, and in 8834 parts of boiling water (Expt. No. 26). The solution has a barely perceptible alkaline reaction. In water containing ammonia and carbonate of ammonia, it dissolves much more sparingly, one part of the salt requiring about 65000 parts (Expt. No. 27); this solution is not precipitated by oxalate of ammonia. Presence of chloride of ammonium and of nitrate of ammonia increases the solubility of carbonate of lime; but the salt is precipitated again from these solutions by ammonia and carbonate of ammonia, and more completely than carbonate of baryta under similar circumstances. Neutral salts of potassa and soda likewise increase its solubility. The precipitation of lime by alkaline carbonate is completely prevented or considerably interfered with by the presence of alkaline citrates (SPILLER) or metaphosphates (RUBE). Water impregnated with carbonic acid dissolves carbonate of lime as bicarbonate. Carbonate of lime remains unaltered in the air, at 100°, and even at a low red heat; but upon the application of a stronger heat, more particularly with free access of air, it gradually loses its carbonic acid. By means of a gas blowpipe-lamp, carbonate of lime (about 0·5 grm.), in an open platinum crucible, is without difficulty reduced to the caustic state; attempts to effect complete reduction over a spirit lamp with double draught have, however, failed (Expt. No. 28). It is decomposed far more readily when mixed with charcoal and heated to redness, giving off its carbonic acid in the form of carbonic oxide.

CaO	28	56·00
CO_2	22	44·00
	50	100·00

c. Oxalate of lime, precipitated from hot or concentrated solutions, is a fine white powder consisting of extremely minute indistinct crystals, and almost absolutely insoluble in water. If the oxalic acid is held to be bibasic, the salt has the formula, $2\ CaO, C_4\ O_6 + 2\ aq$. When precipitated from cold, extremely dilute solutions, the salt presents a more distinctly crystalline appearance, and consists of a mixture of $2\ CaO, C_4\ O_6 + 2\ aq$. and $2\ CaO, C_4\ O_6 + 6\ aq$. (SOUCHAY and LENSSEN). Presence of free oxalic acid and acetic acid slightly increases the solubility of oxalate of lime. The stronger acids (hydrochloric acid, nitric acid) dissolve it readily; from these solutions it is precipitated again, unaltered, by alkalies; and also (provided the excess of acid be not too great) by alkaline oxalates or alkaline acetates added in excess. Oxalate of lime does not dissolve in solutions of chloride of potassium, chloride of sodium, chloride of ammonium, chloride of barium, chloride of calcium, and chloride of strontium, even though these solutions be hot and concentrated; but, on the other hand, it dissolves readily and in appreciable quantities, in hot solutions of the salts belonging to the magnesia group. From these solutions it is reprecipitated by an excess of alkaline oxalate (SOUCHAY and LENSSEN). Alkaline citrates (SPILLER) and metaphosphates (RUBE) impede the precipitation of lime by alkaline oxalates. When treated with solutions of many of the heavy metals, *e.g.*, with solution of chloride of copper, nitrate of silver, &c., oxalate of lime suffers decomposition, a soluble salt of lime being formed, and an oxalate of the heavy metallic oxide, which separates immediately, or after some time (REYNOSO). Oxalate of lime is unalterable in the air, and at 100°. Dried at the latter temperature, it has invariably the following composition (Expt. No. 29, and also SOUCHAY and LENSSEN *):

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* Journ. f. prakt. Chem., 83, 485.

$2\ CaO$	56	38·36
$C_4\ O_6$	72	49·32
2 aq	18	12·32
	146	100·00

At 205° oxalate of lime loses its water, without undergoing decomposition; at a somewhat higher temperature, still scarcely reaching dull redness, the anhydrous salt is decomposed, without actual separation of carbon, into carbonic oxide and carbonate of lime. The powder, which was previously of snowy whiteness, transiently assumes a gray color in the course of this process, even though the oxalate be perfectly pure. Upon continued application of heat, this gray color disappears again. If the oxalate of lime is heated in small coherent fragments, such as are obtained upon drying the precipitated salt on a filter, the commencement and progress of the decomposition can be readily traced by this transient appearance of gray. If the process of heating be conducted properly, the residue will not contain a trace of caustic lime. Hydrated oxalate of lime exposed suddenly to a dull red heat, is decomposed with considerable separation of carbon.

§ 74.

4. MAGNESIA.

Magnesia is weighed as SULPHATE OF MAGNESIA, PYROPHOSPHATE OF

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* Annal. der Chem. und Pharm., 100, 322.

MAGNESIA, OR PURE MAGNESIA. To convert it into the pyrophosphate, it is precipitated as PHOSPHATE OF AMMONIA AND MAGNESIA.

a. Anhydrous *sulphate of magnesia* is a white opaque mass. It dissolves readily in water. It is nearly altogether insoluble in absolute alcohol, but it is somewhat soluble in spirit of wine. It does not alter vegetable colors. Exposed to the air, it absorbs water rapidly. At a moderate red heat, it remains unaltered; but when heated to intense redness, it undergoes partial decomposition, losing part of its acid, after which it is no longer perfectly soluble in water. By means of a blast-lamp, it is tolerably easy to expel the whole of the sulphuric acid from small quantities of sulphate of magnesia (Expt. No. 30). Ignited with chloride of ammonium, sulphate of magnesia is not decomposed.

$Mg\,O$	20	33·33
$S\,O_3$	40	66·67
	60	100·00

b. Phosphate of magnesia and ammonia is commonly a white crystalline powder. [Sometimes it appears as a scaly precipitate with pearly lustre, sometimes in acicular crystals.] It dissolves, at the common temperature, in 15293 parts of cold water (Expt. No. 31). In water containing ammonia, it is much more insoluble—one part of the salt requiring about 45000 parts of the solvent (Expt. No. 32). Chloride of ammonium slightly increases its solubility (Expt. Nos. 34 and 35). Presence of alkaline phosphates exercises no influence in this respect. It dissolves readily in acids, even in acetic acid. Its composition is expressed by the formula

$$2\,Mg\,O,\,N\,H_4\,O,\,P\,O_5 + 12\ aq.$$

10 eq. of water escape at 100°, the remaining 2, together with the ammonia, at a red heat, leaving $2\,Mg\,O,\,P\,O_5$. The change of the ordinary phosphoric to pyrophosphoric acid, is indicated by a vivid incandescence of the whole mass.

If phosphate of magnesia and ammonia is dissolved in dilute hydrochloric or nitric acid, and ammonia be then added to the solution, the salt is reprecipitated completely, or more correctly, only so much remains in solution as corresponds to its ordinary solubility in water containing ammonia and ammoniacal salt (Expt. No. 33).

c. Pyrophosphate of magnesia presents the appearance of a white mass, often slightly inclining to gray. It is barely soluble in water, but readily so in hydrochloric acid, and in nitric acid. It remains unaltered in air, and at a red heat; at a very intense heat it fuses unaltered. Exposed at a white heat to the action of hydrogen, $3\,Mg\,O,\,P\,O_5$ is formed, while $P\,H_3$, P and $P\,O_3$ escape. $3\,(2\,Mg\,O,\,P\,O_5) = 2\,(3\,Mg\,O,\,P\,O_5) + P\,O_5$ (STRUVE*). It leaves the color of moist turmeric-, and of reddened litmus-paper unchanged.

If we dissolve pyrophosphate of magnesia in hydrochloric or nitric acid, add water to the solution, boil for some time, and then precipitate with ammonia in excess, we obtain a precipitate of phosphate of magnesia and ammonia which, after ignition, affords less $2\,Mg\,O,\,P\,O_5$, than was originally employed. WEBER gives the loss as from 1·3 to 2·3 per cent. My own experiments (No. 36) confirm this statement, and point out the circumstances under which the loss is the least considerable. By long-continued fusion with mixed carbonates of potassa and soda, pyrophosphate of magnesia is completely decomposed, the phosphoric acid being reconverted into the tribasic state. If, therefore, we treat the fused mass with hydrochloric acid, and then add water and ammonia, we re-obtain on igniting the precipitate the whole quantity of the salt used.

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* Journ. f. prakt. Chem., 79, 349.

2 MgO	40·00	36·04
PO_5	71·00	63·96
	111·00	100·00

d. Pure magnesia is a white, light, loose powder. It dissolves in 55368 parts of cold, and in the same proportion of boiling water (Expt. No. 37). Its aqueous solution has a very slightly alkaline reaction. Magnesia dissolves in hydrochloric and in other acids, without evolution of gas. Magnesia dissolves readily and in quantity in solutions of neutral ammonia salts, and also in solutions of chloride of potassium and chloride of sodium it is more soluble than in water (Expt. No. 38). Exposed to the air, it slowly absorbs carbonic acid and water. Magnesia is highly infusible, remaining unaltered at a strong red heat, and fusing superficially only at the very highest temperature.

Mg	12	60·03
O	8	39·97
	20	100·00

BASES OF THE THIRD GROUP.

§ 75.

1. ALUMINA.

Alumina is usually precipitated as HYDRATE, occasionally as basic acetate or basic formiate, and is always weighed in the pure state.

a. Hydrate of alumina, recently precipitated, is gelatinous; it invariably retains a minute proportion of the acid with which the alumina was previously combined, as well as of the alkali which has served as the precipitant; it is freed with difficulty from these admixtures by repeated washing.*

Hydrate of alumina is insoluble in pure water; but it readily dissolves in soda and potassa; it is sparingly soluble in caustic ammonia, and altogether insoluble in carbonate of ammonia; presence of ammonical salts greatly diminishes its solubility in caustic ammonia (Expt. No. 39). The correctness of this statement has been amply confirmed by MALAGUTI and DUROCHER;† and also by experiments made by my former assistant, MR. J. FUCHS. The former chemists state also that when a solution of alumina is precipitated with sulphide of ammonium, the fluid may be filtered off five minutes after, without a trace of alumina in it. FUCHS did not find this to be the case (Expt. No. 40).

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* See page note

† Ann. de Chim. et de Phys., 3 Sér. 16, 421.

Hydrate of alumina, recently precipitated, dissolves readily in hydrochloric or nitric acid; but after filtration, or after having remained for some time in the fluid from which it has been precipitated, it does not dissolve in these acids without considerable difficulty and long digestion. Hydrate of alumina shrinks considerably on drying, and then presents the appearance of a hard, transparent, yellowish, or of a white, earthy mass. When heated to redness it loses its water, and this loss is frequently attended with slight decrepitation, and invariably with considerable diminution of bulk.

b. Alumina, prepared by heating the hydrate to a moderate degree of redness, is a loose and soft mass; but upon the application of a very intense degree of redness, it concretes into small, hard lumps. At the most intense white heat it fuses to a colorless glass. Ignited alumina is dissolved by dilute acids with very great difficulty; in fuming hydrochloric acid it dissolves upon long-continued digestion in a warm place, slowly, but completely. It dissolves tolerably easily and quickly by first heating with a mixture of 8 parts of concentrated sulphuric acid and 3 parts of water, and then adding water (A. Mitscherlich[*]). Ignition in a current of hydrogen gas leaves it unaltered. By fusion with bisulphate of potassa it is rendered soluble, the residue dissolving readily in water. Upon igniting alumina with chloride of ammonium, chloride of aluminium escapes; but the process fails to effect complete volatilization of the alumina (H. Rose). When alumina is fused at a very high temperature, in conjunction with ten times its quantity of carbonate of soda, aluminate of soda is formed, which is soluble in water (R. Richter). Placed upon moist red litmus paper, pure alumina does not change the color to blue.

Al_2	27·50	53·40
O_3	24·00	46·60
	51·50	100·00

c. If to the solution of a salt of alumina, carbonate of soda or carbonate of ammonia be added, till the resulting precipitate only just redissolves on stirring, and then acetate of soda or acetate of ammonia poured in in abundance and the mixture boiled some time, the alumina is precipitated almost completely as basic acetate in the form of transparent flocks, so that if the filtrate be boiled with chloride of ammonium and ammonia only unweighable traces of alumina separate. If the quantity of acetate of soda employed be too small, the precipitate appears more granular, the filtrate would then contain a larger amount of alumina. The precipitate is difficult to filter or wash. In washing it it is best to use boiling water, containing a little acetate of soda or acetate of ammonia. The precipitate is readily soluble in hydrochloric acid.

d. If, instead of the acetates mentioned in *c*, the corresponding formiates be used, a flocculent voluminous precipitate of basic formiate of alumina is obtained, which may be very readily washed (Fr. Schulze[†]).

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[*] Journ. f. prakt. Chem., 81, 110.

[†] Chem. Centralbl., 1861, 3.

§ 76.

2. SESQUIOXIDE OF CHROMIUM.

Sesquioxide of chromium is usually precipitated as HYDRATE, and always weighed in the pure state.

a. Hydrated sesquioxide of chromium, recently precipitated from a green solution, is greenish-gray, gelatinous, insoluble in water: it dissolves readily, in the cold, in solutions of potassa or soda, to a dark green fluid; it dissolves also in the cold, but rather sparingly, in solution of ammonia, to a bright violet red fluid. In acids it dissolves readily, imparting a dark green tint to the fluid. Presence of chloride of ammonium exercises no influence upon the solubility of the hydrate in ammonia. Boiling effects the complete separation of the sesquioxide from its solutions in potassa, soda, or ammonia (Expt. No. 41). The dried hydrate is a greenish-blue powder; it loses its water at a gentle red heat.

b. Sesquioxide of chromium, produced by heating the hydrate to dull redness, is a dark green powder; upon the application of a higher degree of heat it assumes a lighter tint, but suffers no diminution of weight; the transition from the darker to the lighter tint is marked by a vivid incandescence of the powder. The feebly ignited sesquioxide is difficultly soluble in hydrochloric acid, and the strongly ignited sesquioxide is altogether insoluble in that acid. Mixed with chloride of ammonium, and exposed to a red heat, sesquioxide of chromium remains unaltered; it suffers no alteration when ignited in a current of hydrogen gas.

Cr_2	52·48	68·62
O_3	24·00	31·38
	76·48	100·00

BASES OF THE FOURTH GROUP.

§ 77.

1. OXIDE OF ZINC.

Zinc is weighed in the form of OXIDE or SULPHIDE; it is precipitated as BASIC CARBONATE, or as SULPHIDE.

a. Basic carbonate of zinc, recently precipitated, is white, flocculent, nearly insoluble in water—(one part requiring 44600 parts. Expt. No. 42)—but readily soluble in potassa, soda, ammonia, carbonate of ammonia, and acids. The solutions in soda or potassa, if concentrated, are not altered by boiling; but if dilute, nearly all the oxide of zinc present is thrown down, as a white precipitate. From the solutions in ammonia and carbonate of ammonia, especially if they are dilute, oxide of zinc likewise separates upon boiling. When a neutral solution of zinc is precipitated with carbonate of soda or carbonate of potassa, carbonic acid is evolved, since the precipitate formed is not $Zn\,O, CO_2$, but consists of a compound of hydrated oxide of zinc with carbonate of zinc, in varying proportions, according to the degree of concentration of the solution, and to the mode of precipitation. Owing to the presence and action of this carbonic acid, part of the oxide of zinc remains in solution; if filtered cold, therefore, the filtrate gives a precipitate with sulphide of ammonium.

But if the solution is precipitated boiling, and kept at that temperature for some time, the precipitation of the zinc is complete to the extent that the filtrate is not rendered turbid by the addition of sulphide of ammonium; still, if the filtrate, mixed with sulphide of ammonium, be allowed to stand at rest for many hours, minute and almost unweighable flakes of sulphide of zinc will separate from the fluid. The precipitate of carbonate of zinc, obtained in the manner just described, may be completely freed from all admixture of alkali by washing with hot water. If ammoniacal salts be present, the precipitation is not complete till every trace of ammonia is expelled. If the solution of a zinc salt is mixed with carbonate of potassa or soda in excess, the mixture evaporated to dryness, at a gentle heat, and the residue treated with cold water, a perceptible proportion of the zinc is obtained in solution as double carbonate of zinc and potassa or soda; but if the mixture is evaporated to dryness at boiling heat, and the residue treated with hot water, the whole of the zinc, with the exception of an extremely minute proportion, as we have already had occasion to observe, is obtained as carbonate of zinc.

The dried basic carbonate of zinc is a fine, white, loose powder; exposure to a red heat converts it into oxide of zinc.

b. Oxide of zinc, produced from the carbonate by the application of a red heat, is a white light powder, with a slightly yellow tint. When heated, it acquires a yellow color, which disappears again on cooling. Upon ignition with charcoal, carbonic oxide gas and zinc fumes escape. By igniting in a rapid current of hydrogen gas, metallic zinc is produced; whilst by igniting it in a feeble current of hydrogen gas, crystallized oxide of zinc is obtained (ST. CLAIRE DEVILLE). In this case, too, a portion of the metal is reduced and volatilized. Oxide of zinc is insoluble in water. Placed on moist turmeric paper, it does not change the color to brown. In acids, oxide of zinc dissolves readily and without evolution of gas. Ignited with chloride of ammonium, fused chloride of zinc is produced, which volatilizes with very great difficulty, if the air is excluded; but readily and completely with free access of air, and with chloride of ammonium fumes. Mixed with a sufficiency of powdered sulphur and ignited in a stream of hydrogen, the corresponding amount of sulphide is obtained (H. ROSE).

Zn................	32·53	80·26
O.................	8·00	19·74
	40·53	100·00

c. Sulphide of zinc, recently precipitated, is a white, loose hydrate (ZnS, HO). The following facts should here be mentioned with regard to its precipitation.[*] Colorless sulphide of ammonium precipitates dilute solutions of zinc, but only slowly; yellow sulphide of ammonium does not precipitate dilute solutions of zinc (1 : 5000) at all. Chloride of ammonium favors the precipitation considerably. Free ammonia acts so as to keep the precipitate somewhat longer in suspension, otherwise it exerts no injurious influence. If the conditions which I shall lay down are strictly observed, oxide of zinc may be precipitated by sulphide of ammonium from a solution containing only $\frac{1}{800000}$. Hydrated sulphide of zinc, on account of its slimy nature, easily stops up the pores of the filter, and cannot therefore be washed without difficulty on a filter. The washing is best performed by using water containing sulphide of ammonium, and continually diminished quantities of chloride of ammonium (at last none) (see Expt. No. 43). The hydrate is insoluble in water, in caustic alkalies, alkaline carbonates, and the monosulphides of the alkali metals. It dissolves readily and completely in hydrochloric and in nitric, but only very sparingly in acetic acid. When dried, the precipitated sulphide of zinc is a white powder; at 100° it loses half, and at a red heat the whole of its water. During the latter process some sulphuretted hydrogen escapes, and the remaining sulphide of zinc contains an admixture of oxide of zinc. By roasting in the air, and intense ignition of the residue, small quantities of sulphide of zinc may be readily converted into the oxide.

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[*] Journ. f. prakt. Chem., 82, 263.

On igniting the dried sulphide of zinc, mixed with powdered sulphur, in a stream of hydrogen, the pure anhydrous sulphide is obtained. (H. ROSE).

Zn	32·53	67·03
S	16·00	32·97
	48·53	100·00

§ 78.

2. PROTOXIDE OF MANGANESE.

Manganese is weighed either as PROTOSESQUIOXIDE, as SULPHIDE, or as PYROPHOSPHATE. With the view of converting it into the first form, it is precipitated as PROTOCARBONATE, HYDRATED PROTOXIDE, or BINOXIDE. Before weighing as pyrophosphate it must be precipitated as AMMONIO-PHOSPHATE.

a. Carbonate of protoxide of manganese, recently precipitated, is white, flocculent, nearly insoluble in pure water, but somewhat more soluble in water impregnated with carbonic acid. Presence of carbonate of soda or potassa does not increase its solubility. Recently precipitated carbonate of protoxide of manganese dissolves pretty readily in solution of chloride of ammonium: it is owing to this property that a solution of protoxide of manganese cannot be completely precipitated by carbonate of potassa or soda, in presence of chloride of ammonium (or any other ammoniacal salt), until the latter is completely decomposed. If the precipitate, while still moist, is exposed to the air, or washed with water impregnated with air, especially if it is in contact with carbonated alkali, it slowly assumes a dirty brownish-white color, part of it becoming converted into hydrated protosesquioxide of manganese. In washing the precipitate, we often obtain a turbid filtrate. If the latter be allowed to stand for some time in a warm place, the manganese separates in brown flocks. If the precipitate is dried out of contact with air, it forms a delicate white powder, persistent in the air [$2\,(Mn\,O, C\,O_2) + aq.$]; but when dried with free access of air, the powder is of a more or less dirty-white color. When strongly heated with access of air, this powder first turns black, and changes subsequently to brown protosesquioxide of manganese. However, this conversion takes some time, and must never be held to be completed until two weighings, between which the precipitate has been ignited again with free access of air, give perfectly corresponding results. On igniting the carbonate of manganese, mixed with powdered sulphur, in a stream of hydrogen, sulphide of manganese is obtained (H. Rose).

b. Hydrated protoxide of manganese, recently thrown down, forms a white, flocculent precipitate, insoluble in water and in the alkalies, but soluble in chloride of ammonium; this precipitate immediately absorbs oxygen from the air, and turns brown, owing to the formation of hydrated protosesquioxide of manganese. On drying it in the air, a brown powder (hydrated protosesquioxide of manganese) is obtained, which, when heated to intense redness, with free access of air, is converted into protosesquioxide of manganese, and on ignition with powdered sulphur, in a stream of hydrogen, is converted into sulphide.

c. Protosesquioxide of manganese, artificially produced, is a brown powder. All the oxides of manganese are finally converted into this by ignition in the air. Each time it is heated it assumes a darker color, but its weight remains unaltered. It is insoluble in water, and does not alter vegetable colors. Heated to redness with chloride of ammonium it is converted into protochloride of manganese. When heated with concentrated hydrochloric acid, it dissolves to chloride with evolution of chlorine.

$$(Mn_3\ O_4+4\ H\ Cl=3\ Mn\ Cl+Cl+4\ H\ O)$$

On ignition with powdered sulphur in a stream of hydrogen it is converted into sulphide (H. Rose).

Mn_3	82·50	72·05
O_4	32·00	27·95
	114·50	100·00

d. Binoxide of manganese is often produced in analysis by exposing a concentrated solution of nitrate of protoxide of manganese to a gradually increased temperature. At 140° brown flakes separate, at 155° much nitric acid is disengaged, and the whole of the manganese separates as anhydrous binoxide. It is brownish black and is deposited on the sides of the vessel, with metallic lustre. It is insoluble in weak nitric acid, but dissolves to a small amount in hot and concentrated nitric acid (Deville). In hydrochloric acid it dissolves with evolution of chlorine, in concentrated sulphuric acid with liberation of oxygen. The binoxide is also often obtained in the hydrated condition in analytical separations, thus when we precipitate a solution of protoxide with hypochlorite of soda, or, after addition of acetate of soda, with chlorine in the heat. The brownish-black flocculent precipitate thus obtained is apt to contain alkali.

e. Sulphide of manganese, prepared in the wet way, forms a flesh-colored precipitate. I must make a few remarks with reference to its precipitation.* This is effected but incompletely if we add to a pure manganese solution only sulphide of ammonium, no matter whether it be colorless or yellow, while it is perfectly effected if chloride of ammonium be used in addition. A very large quantity even of chloride of ammonium does not impede the precipitation; the presence of a large quantity of free ammonia somewhat interferes with the completeness of the precipitation. In all cases we must allow to stand at least 24 hours, and with very dilute solutions 48 hours, before filtering. The yellow sulphide of ammonium is the most appropriate precipitant. In the presence of chloride of ammonium even a large excess of sulphide of ammonium is uninjurious. If the precipitation is conducted as directed, the manganese can be precipitated from solutions which contain only $\frac{1}{100000}$ of the protoxide. If the flesh-colored hydrated sulphide remains some time under the fluid from which it was precipitated, it sometimes becomes converted into the green anhydrous sulphide. This appearance often occurs after a few hours or days, sometimes not for weeks. In acids (hydrochloric, sulphuric, acetic, &c.) the hydrate dissolves with evolution of sulphuretted hydrogen. If the precipitate, while still moist, is exposed to the air, or washed with water impregnated with air, its fleshy tint changes to brown, hydrated protosesquioxide of manganese being formed, together with a small portion of sulphate of protoxide of manganese. Hence in washing the hydrate we always add some sulphide of ammonium to the wash-water, and keep the filter as full as possible with the same. We guard against the filtrate running through turbid, by adding gradually decreasing quantities of chloride of ammonium to the wash-water (at last none). (Expt. No. 44.) On igniting the precipitate mixed with sulphur in a stream of hydrogen the anhydrous sulphide remains. If we have gently ignited during this process, the product is light green; if we have strongly ignited, it is dark green to black. Neither the green nor the black sulphide attracts oxygen or water quickly from the air (H. ROSE).

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* Journ. f. prakt. Chem., 82, 265.

Mn	27·5	63·22
S	16·0	36·78
	43·5	100·00

[*f. Ammonio-phosphate of manganese* is at first a white, semi-gelatinous precipitate, which, on standing for some time in the cold, and more speedily at the boiling point, crystallizes in pale rose-colored pearly scales. It dissolves easily in hydrochloric or nitric acid, but is almost absolutely insoluble in boiling water, ammonia, and ammoniacal salts, and may be washed with facility. Its formula is:

$$2\,MnO,\ NH_4O,\ PO_5\ 2\,HO.$$

By ignition it is converted into pyrophosphate of manganese.

g. Pyrophosphate of manganese is a nearly white powder, not altered by a full red heat or by exposure to the air.

2 Mn O	71	50
PO_5	71	50
	142	100]

§ 79.

8. PROTOXIDE OF NICKEL.

Nickel is precipitated as HYDRATED PROTOXIDE, HYDRATED SESQUIOXIDE, and as SULPHIDE. It is weighed in the form of PROTOXIDE.

a. Hydrated protoxide of nickel forms an apple-green precipitate, almost absolutely insoluble in water, but soluble in ammonia and carbonate of ammonia. From these solutions it is completely reprecipitated by potassa or soda, added in excess; application of heat promotes the precipitation. It is unalterable in the air; on intense ignition, it passes into pure anhydrous protoxide.

b. Protoxide of nickel is a dirty grayish-green powder, insoluble in water, but readily soluble in hydrochloric acid. It does not affect vegetable colors. It suffers no variation of weight upon ignition with free access of air. It is easily reduced to metallic nickel by ignition in hydrogen gas.

Ni	29·5	78·67
O	8·0	21·33
	37·5	100·00

[*c. Hydrated sesquioxide of nickel*, thrown down by caustic soda from solutions of nickel which have been mixed with solution of hypochlorite of soda, is a black precipitate that is much more easily washed than the hydrated protoxide. It passes into protoxide upon ignition.]

d. Hydrated sulphide of nickel, prepared in the wet way, forms a black precipitate, insoluble in water. When thrown down in the cold it is somewhat soluble in sulphide of ammonium containing free ammonia, the supernatant liquid having a brown color. The cold precipitated sulphide is liable to oxidize somewhat on the filter to sulphate of nickel. [When separated from boiling solutions by sulphide of sodium, as is directed § 110, these inconveniences are not experienced.] It is very sparingly soluble in concentrated acetic acid, somewhat more soluble in hydrochloric acid. It is more readily soluble still in nitric acid, but its best solvent is nitrohydrochloric acid. It loses its water upon the application of a red heat; when ignited in the air, it is transformed into a basic compound of sesquioxide of nickel with sulphuric acid. Mixed with sulphur and ignited in a stream of hydrogen, a fused mass remains, of pale-yellow color and metallic lustre. This consists of Ni_2S, but its composition is not perfectly constant (H. Rose).

§ 80.

4. Protoxide of Cobalt.

Cobalt is weighed in the PURE METALLIC state, or as PROTOXIDE; or as SULPHATE OF PROTOXIDE, or as NITRITE OF COBALT AND POTASSA. Besides the properties of these substances, we have to study here also those of the HYDRATED PROTOXIDE, of the HYDRATED SESQUIOXIDE, and of the SULPHIDE.

a. Hydrated protoxide of cobalt.—Upon precipitating a solution of protoxide of cobalt with potassa, a blue precipitate (a basic salt) is formed at first, which, upon boiling with potassa in excess, excluded from contact of air, changes to light red hydrated protoxide of cobalt; if, on the contrary, this process is conducted with free access of air, the precipitate becomes discolored, part of the hydrated protoxide being converted into hydrated sesquioxide. The hydrate, prepared in this way, retains a trace of the acid, and, even after the most thorough washing with hot water, also a minute amount of the alkaline precipitant (Expt. No. 46).

Hydrated protoxide of cobalt is insoluble in water, and also in potassa;

it dissolves in solutions of ammoniacal salts; when dried in the air it absorbs oxygen, and acquires a brownish color. (See *b.*)

[*b. Protoxide of cobalt.*—Hydrated protoxide of cobalt, when ignited in the air or in oxygen, yields a variable mixture of protoxide and protosesquioxide, and cannot certainly be brought to a constant composition. If, however, it be intensely ignited, and cooled in a stream of carbonic acid, it leaves pure protoxide of cobalt (RUSSEL,* GAUHE,† BURTON‡). The protoxide has a light-brown color; is but slightly hygroscopic, and dissolves in hydrochloric acid without evolving chlorine.

Co	29·50	78·67
O	8·00	21·33
	37·50	100·00]

[*c. Hydrated sesquioxide of cobalt* is thrown down from solutions of protosalts of cobalt by a mixture of potassa and hypochlorite of soda as a brown-black precipitate, which is completely insoluble in the precipitants and in hot water, and may be washed from all but the minutest traces of alkali with much greater ease than the hydrated protoxide. (See *d.*)]

Co_3	88·5	73·44
O_4	32·0	26·56
	120·5	100·00

d. Metallic cobalt is obtained from any and all its oxides, and from the nitrate and chloride of cobalt, by ignition in a current of hydrogen gas. It is a grayish-black magnetic powder, less fusible than gold. If the reduction has been effected at an intense red heat, the metal is unalterable in the air; if at a low heat, it oxidizes or even burns. Metallic cobalt does not decompose water, either cold or boiling; it dissolves in nitric and sulphuric acids to the corresponding salts of protoxide.

[Metallic cobalt, obtained from oxides which have been precipitated by caustic alkalies, has an alkaline reaction, from the retention by the oxides of a trace of alkali. This alkali, which need not exceed 0·2–0·3 per cent., may be removed by repeated washings of the metal with hot water.]

e. Sulphide of cobalt, produced in the wet way, forms a black precipitate, insoluble in water, in alkalies, and in alkaline sulphides. When precipitated cold, and exposed moist to the air, it oxidizes to sulphate. [If the precipitate be digested hot, or made with hot sulphide of sodium, as directed § 111, it washes readily and without danger of oxidation.] Sulphide of cobalt is but sparingly soluble [if precipitated hot, insoluble] in acetic acid and in dilute mineral acids, more readily in concentrated mineral acids, and most readily in warm nitro-hydrochloric acid. [Sulphide of cobalt may be converted into sulphate by heating with strong nitric acid.] Mixed with sulphur and ignited in a stream of hydrogen, we obtain a product of uncertain composition, not suited for the determination of cobalt (H. ROSE).

f. Sulphate of protoxide of cobalt crystallizes, in combination with

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* Jour. Chem. Soc. (2), I. 51.

† Fres. Zeitschrift, IV. 55.

‡ Private communication.

7 aq., slowly in oblique rhombic prisms of a fine red color. The crystals yield the whole of the 7 eq. of water at a moderate heat, and are converted into a rose-colored anhydrous salt, which bears the application of a gentle red heat for a short time without losing acid. It dissolves rather difficultly in cold, but more readily in hot water. [By strong ignition in an atmosphere of carbonate of ammonia it may be reduced to metallic cobalt.]

$Co\,O$	37·5	48·39
$S\,O_3$	40·0	51·61
	77·5	100·00

g. Nitrite of cobalt and potassa, which is easily produced by mixing a solution of protoxide of cobalt with nitrite of potassa, and enough nitric or acetic acid to liberate some nitrous acid and make the liquid permanently acid, forms a crystalline precipitate of a fine yellow color, which dissolves to a very perceptible amount in pure water, and still more copiously in water containing chloride of sodium and chloride of ammonium. In rather concentrated solutions of salts of potassa (KO, SO_3, — $K\,Cl$, — $K\,O, N\,O_5$, — $K\,O, \overline{A}$), [containing some nitrite of potassa (GAUHE)], it is insoluble even upon boiling.[*] The presence of a *small* proportion of free acetic acid exercises no solvent action under these circumstances. The precipitate does not dissolve in alcohol of 80 per cent.; but it dissolves, though not copiously, in boiling water, to a red fluid. Nitrite of cobalt and potassa is decomposed with difficulty by solution of potassa, but readily by solution of soda, or by baryta-water; the decomposition is attended with separation of brown hydrated sesquioxide of cobalt (A. STROMEYER[†]). [The composition, dried at 100°, is somewhat variable (STROMEYER, ERDMANN[‡]).

$Co_2\,O_3$ (?)	17·7 — 19·0
KO	28·2 — 32·8
N	15·8 — 17·8
Water	3·9 — 5·8].

It is decomposed by ignition, and gives protosesquioxide of cobalt and potassa. [In presence of nickel and alkaline earths the precipitate contains nickel (ERDMANN)].

§ 81.

5. PROTOXIDE OF IRON; and 6. SESQUIOXIDE OF IRON.

Iron is usually weighed in the form of SESQUIOXIDE, occasionally as SULPHIDE. We have to study also the HYDRATED SESQUIOXIDE, the SUCCINATE OF THE SESQUIOXIDE, the ACETATE OF THE SESQUIOXIDE, and the FORMIATE OF THE SESQUIOXIDE.

a. Hydrated sesquioxide of iron, recently prepared, is a reddish-brown precipitate, insoluble in water, in the alkalies, and in ammoniacal salts, but

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[[*] If thrown down in absence of free acid the precipitate has a darker color, and is soluble to a slight degree in solution of acetate of potassa.]

[†] Annal. d. Chem. u. Pharm., 96, 218.

[‡] Jour. f. prakt. Chem., 97, 385.

readily soluble in acids; the process of drying very greatly reduces the bulk of this precipitate. When dry, it presents the appearance of a brown, hard mass, with shining conchoidal fracture. If the precipitant alkali is not used in excess, the precipitate contains basic salt; on the other hand, if the alkali has been used in excess, a portion of it is invariably carried down, in combination with the sesquioxide of iron,—on which account ammonia alone can properly be used in analysis, as a precipitant for salts of sesquioxide of iron. Under certain circumstances, for instance, by protracted heating of a solution of acetate of sesquioxide of iron on the water-bath (which turns the solution from blood-red to brick-red, and makes it appear turbid by reflected light), and subsequent addition of some sulphuric acid or salt of an alkali, a reddish-brown hydrate is produced, which is insoluble in cold acids, even though concentrated, and is not attacked even by boiling nitric acid (L. PEAN DE St. GILLES*).

b. The hydrated sesquioxide of iron is, upon ignition, converted into the *anhydrous sesquioxide.* If the hydrated sequioxide has not been most carefully and thoroughly dried, the small solid lumps, though dry outside, retain still a portion of water confined within, the sudden conversion of that water into steam, upon the application of a red heat, will cause particles of the sesquioxide to fly about, and may thus lead to loss of substance. Pure sesquioxide of iron, when placed upon moist reddened litmus paper, does not change the color to blue. It dissolves slowly in dilute, but more rapidly in concentrated hydrochloric acid; the application of a moderate degree of heat effects this solution more readily than boiling. With a mixture of 8 parts concentrated sulphuric acid and 3 parts water, it behaves in the same manner as alumina.

The weight of the sesquioxide does not vary upon ignition in the air; when ignited together with chloride of ammonium, sesquichloride of iron escapes. Ignition with charcoal, in a closed vessel, reduces it more or less. Strongly ignited with sulphur in a stream of hydrogen, it is transformed into protosulphide.

Fe_2	56	70·00
O_3	24	30·00
	80	100·00

c. Sulphide of iron, produced in the humid way, forms a black precipitate. The following facts are to be noticed with regard to its precipitation.† Sulphide of ammonium used alone, whether colorless or yellow, precipitates pure neutral solutions of protoxide of iron, but slowly and imperfectly. Chloride of ammonium acts very favorably; a large excess even is not attended with incovenience. Ammonia has no injurious action. It is all the same whether the sulphide of ammonium be colorless or light yellow. If the directions given are observed, iron may be precipitated by means of sulphide of ammonium from solutions containing only $\frac{1}{1600000}$ of the protoxide. In such a case, however, it is necessary to allow to stand forty-eight hours. Since the precipitate rapidly oxidizes in contact with air, sulphide of ammonium is to be added to the wash-water, and the filter kept full. [By keeping the precipitate with the liquid near the boiling point for a long time (48 hours), adding sulphide of ammonium from time to time, the sulphide of iron becomes dense, and may be washed with little danger of oxidation.] It is well to mix a little chloride of ammonium with the wash-water, but the quantity should be continually reduced, and the last water used should contain none. In mineral acids, even when very dilute, the hydrated sulphide dissolves readily. Mixed with sulphur, and strongly ignited in a stream of hydrogen, anhydrous protosulphide remains (H. Rose).

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* Journ. f. prakt. Chem., 66, 137.

† Ibid., 82, 268.

Fe............	28	63·64
S.............	16	36·36
	44	100·00

d. When a neutral solution of a salt of sesquioxide of iron is mixed with a neutral solution of an alkaline succinate, a cinnamon-colored precipitate of a brighter or darker tint is formed; this is *succinate of sesquioxide of iron* ($Fe_2 O_3, C_8 H_4 O_6$). It results from the nature of this precipitate, that its formation must set free an equivalent of acid (succinic acid, if the succinate of ammonia is used in excess); *e.g.*, $2 (Fe_2 O_3, 3 S O_3) + 3 (2 N H_4 O, C_8 H_4 O_6) + 2 H O = 2 (Fe_2 O_3, C_8 H_4 O_6) + 6 (N H_4 O, S O_3) + 2 H O, C_8 H_4 O_6$. The free succinic acid does not exercise any perceptible solvent action upon the precipitate in a cold and highly dilute solution, but it redissolves the precipitate a little more readily in a warm solution. The precipitate must therefore be filtered cold, if we want to guard against re-solution. Succinate of sesquioxide of iron is insoluble in cold, and but sparingly soluble in hot water. It dissolves readily in mineral acids. Ammonia deprives it of the greater portion of its acid, leaving compounds similar to the hydrated sesquioxide of iron, which contain from 18 to 30 eq. $Fe_2 O_3$ for 1 eq. $C_8 H_4 O_6$ (Döpping). Warm ammonia withdraws the acid more completely than cold ammonia.

[*e.* If to a hot solution of a salt of sesquioxide of iron carbonate of soda be added till a slight permanent precipitate is formed, and this be redissolved by a few drops of hydrochloric acid, then heated to boiling, and crystals of acetate of soda be added, the whole of the iron will be precipitated as *basic acetate of sesquioxide.* The success of this operation depends on the iron solution being sufficiently dilute, the free acid sufficiently neutralized, and the acetate of soda in sufficient quantity. Instead of carbonate and acetate of soda the corresponding salts of ammonia may be used. The precipitate may usually be filtered off and washed without any iron passing into the filtrate; sometimes, however, the reverse is the case. It is best to filter immediately, and to use boiling wash-water. When these directions are followed, the precipitate is free from alkali, but if the precipitate is digested with the liquid, it fixes alkali and becomes more difficult to work* (Reichardt)].

f. Instead of the acetate of soda or ammonia used in *e*, the corresponding formiates may be used. The basic *formiate of sesquioxide of iron* here obtained is more easily washed than the basic acetate (Fr. Schulze †).

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* Fres. Zeitschrift, V. 63.

† Chem. Centralbl., 1861, 3.

BASES OF THE FIFTH GROUP.

§ 82.

1. OXIDE OF SILVER.

Silver may be weighed in the METALLIC state, as CHLORIDE, SULPHIDE, or CYANIDE.

a. Metallic silver, obtained by the ignition of salts of silver with organic acids, &c., is a loose, light, white, glittering mass of metallic lustre; but, when obtained by reducing chloride of silver, &c., in the wet way, by the agency of zinc, it is a dull gray powder. It is not fusible over a BERZELIUS' lamp. Ignition leaves its weight unaltered. It dissolves readily and completely in dilute nitric acid.

b. Chloride of silver, recently precipitated, is white and curdy. On shaking, the large spongy flocks combine with the smaller particles, so that the fluid becomes perfectly clear. This result is, however, only satisfactorily effected, when the flocks have been produced in presence of excess of silver solution, and when they have been recently precipitated (compare G. J. MULDER *). Chloride of silver is in a very high degree insoluble in water and in dilute nitric acid; strong nitric acid, on the contrary, does dissolve a trace. Hydrochloric acid, especially if concentrated and boiling, dissolves it very perceptibly. On sufficiently diluting such a solution with cold water the chloride of silver falls out so completely that the filtrate is not colored by sulphuretted hydrogen. Chloride of silver is insoluble, or very nearly so, in concentrated sulphuric acid; in the dilute acid it is as insoluble as in water. In a solution of tartaric acid chloride of silver dissolves perceptibly on warming; on cooling, however, the solution deposits the whole, or, at all events, the greater part of it. Aqueous solutions of chlorides (of sodium, potassium, ammonium, calcium, zinc, &c.) all dissolve appreciable quantities of chloride of silver, especially if they are hot and concentrated. On sufficient dilution with cold water the dissolved portion separates so completely that the filtrate is not colored by sulphuretted hydrogen. The solutions of alkaline and alkaline earthy nitrates also dissolve a little chloride of silver. The solubility in the cold is trifling; in the heat, on the contrary, it is very perceptible. A solution of nitrate of mercury dissolves chloride of silver to a tolerable extent; alkaline acetates separate it from the solution. Chloride of silver dissolves readily in aqueous ammonia, and also in the solution of cyanide of potassium and that of hyposulphite of soda. Under the influence of light the chloride of silver soon changes to violet, finally black, losing chlorine, and passing partly into $Ag_2 Cl$. The change is quite superficial, but the loss of weight resulting is very appreciable (MULDER, *op. cit.* p. 21). On long contact (say for 24 hours) with pure water, especially if hot of 75°, chloride of silver, although removed from the influence of light, becomes gray, and, it appears, decomposed; the precipitate is found to contain oxide of silver, and the water hydrochloric acid (MULDER). On digestion with excess of solution of bromide or iodide of potassium the chloride of silver is completely transformed into bromide or iodide of silver, as the case may be (FIELD †). On drying, chloride of silver becomes pulverulent; on heating, it acquires a yellow color; at 260° it fuses to a transparent yellow fluid, which on cooling presents the appearance of a colorless and slightly yellowish mass. At a very strong heat it volatilizes unchanged. It may be readily reduced to metallic silver, by igniting it in a current of hydrogen gas.

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* Die Silberprobirmethode, translated into German by D. Chr. Grimm, pp. 19 and 311. Leipzig: J. J. Weber. 1859.

† Quart. Journ. of Chem. Soc. x. 234; Journ. f. prakt. Chem. 73, 404.

Ag	107·97	75·28
Cl	35·46	24·72
	143·43	100·00

c. Sulphide of silver, prepared in the humid way, is a black precipitate, insoluble in water, dilute acids, alkalies, and alkaline sulphides. This precipitate is unalterable in the air; after being allowed to subside, it is filtered and washed with ease, and may be dried at 100°, without suffering decomposition. It dissolves in concentrated nitric acid, with separation of sulphur. Solution of cyanide of potassium fails to dissolve sulphide of silver, except the cyanide be used greatly in excess. In the latter case it dissolves to a slight extent, but is generally reprecipitated on addition of water (Bechamp*). Ignited in a current of hydrogen, it passes readily and completely into the metallic state (H. Rose).

Ag	107·97	87·07
S	16·00	12·93
	123·97	100·00

d. Cyanide of silver, recently thrown down, forms a white curdy precipitate insoluble in water and dilute nitric acid, soluble in cyanide of potassium and also in ammonia; exposure to light fails to impart the slightest tinge of black to it; it may be dried at 100° without suffering decomposition. Upon ignition, it is decomposed into cyanogen gas, which escapes, and metallic silver, which remains, mixed with a little paracyanide of silver. By boiling with a mixture of equal parts of sulphuric acid and water, it is, according to Glassford and Napier, dissolved to sulphate of silver, with liberation of hydrocyanic acid.

Ag	107·97	80·60
C_2N	26·00	19·40
	133·97	100·00

§ 83.

2. Oxide of Lead.

Lead is weighed as OXIDE, SULPHATE, CHROMATE, and SULPHIDE. Besides these compounds, we have also to study the CARBONATE and the OXALATE.

a. Neutral carbonate of lead forms a heavy, white, pulverulent precipitate. It is but very slightly soluble in perfectly pure (boiled) water (one part requiring 50550 parts, see Expt. 47, *a*); but it dissolves somewhat more readily in water containing ammonia and ammoniacal salts (comp. Expt. No. 47, *b* and *c*). It dissolves also somewhat more readily in water impregnated with carbonic acid, than in pure water. It loses its carbonic acid when ignited.

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* Journ. f. prakt. Chem. 60, 64.

b. Oxalate of lead is a white powder, very sparingly soluble in water. The presence of ammonia salts slightly increases its solubility (Expt. No. 48). When heated in close vessels, it leaves suboxide of lead; but when heated, with access of air, yellow oxide (protoxide).

c. Oxide, or *protoxide of lead*, produced by igniting the carbonate or oxalate, is a lemon-yellow powder, inclining sometimes to a reddish yellow, or to a pale yellow. When this yellow oxide of lead is heated, it assumes a brownish-red color, without the slightest variation of weight. It fuses at an intense red heat. Ignition with charcoal reduces it. When exposed to a white heat, it rises in vapor. Placed upon moist reddened litmus paper, it changes the color to blue. When exposed to the air, it slowly absorbs carbonic acid. Mixed with chloride of ammonium and ignited, it is converted into chloride of lead. Oxide of lead in a state of fusion readily dissolves silicic acid and the earthy bases with which the latter may be combined.

Pb............	103·50	92·83
O	8·00	7·17
	111·50	100·00

d. Sulphate of lead is a heavy white powder. It dissolves, at the common temperature, in 22800 parts of pure water (Expt. No. 49); it is less soluble still in water containing sulphuric acid (one part requiring 36500 parts—Expt. No. 50); it is far more readily soluble in water containing ammoniacal salts; from this solution it may be precipitated again by adding sulphuric acid in excess (Expt. No. 51). It is almost entirely insoluble in alcohol and spirit of wine. Of the salts of ammonia, the nitrate, acetate, and tartrate are more especially suited to serve as solvents for sulphate of lead: the two latter salts of ammonia are made strongly alkaline by addition of ammonia, previous to use (WACKENRODER). Sulphate of lead dissolves in concentrated hydrochloric acid, upon heating. In nitric acid it dissolves the more readily, the more concentrated and hotter the acid; water fails to precipitate it from its solution in nitric acid; but the addition of a copious amount of dilute sulphuric acid causes its precipitation from this solution. The more nitric acid the solution contains, the more sulphuric acid is required to throw down the sulphate of lead. Sulphate of lead dissolves sparingly in concentrated sulphuric acid, and the dissolved portion precipitates again upon diluting the acid with water (more completely upon addition of alcohol). A moderately concentrated solution of hyposulphite of soda dissolves the sulphate of lead completely even if cold, more readily if warmed; on boiling, the solution becomes black from separation of a small quantity of sulphide of lead (J. LÖWE *). The solutions of carbonates and bicarbonates of the alkalies convert sulphate of lead, even at the common temperature, completely into carbonate of lead. The solutions of the carbonates, but not those of the bicarbonates, dissolve some oxide of lead in this process (H. ROSE †). Sulphate of lead dissolves readily in hot solutions of potassa or soda. It is unalterable in the air, and at a gentle red heat; when exposed to a higher degree of heat, it fuses without suffering decomposition (Expt. No. 52), provided always the action of reducing gases be completely excluded—for, if this is not the case, the weight will continually diminish, owing to the reduction of PbO, SO_3 to PbS (ERDMANN [*]). Fusion with cyanide of potassium reduces the whole of the lead to the metallic state.

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* Journ. f. prakt. Chem. 74, 348.

† Pogg. Annal. 95, 426.

PbO	111·50	73·60
SO_3	40·00	26·40
	151·50	100·00

e. Sulphide of lead, prepared in the wet way, is a black precipitate, insoluble in water, dilute acids, alkalies, and alkaline sulphides. In precipitating it from a solution containing free hydrochloric acid, it is necessary to dilute plentifully, otherwise the precipitation will be incomplete. Even if a fluid only contain 2·5 per cent. HCl, the whole of the lead will not be precipitated (M. MARTIN [†]). It is unalterable in the air; it cannot be dried at 100° without suffering decomposition. According to H. ROSE it increases perceptibly in weight by oxidation; in the case of long-protracted drying even becoming a few per cents. heavier.[‡] I have confirmed his statement (see Expt. No. 53). If sulphate of lead mixed with sulphur be exposed in a current of hydrogen to a good red heat, pure crystalline PbS remains; if a less heat be employed, the residue contains excess of sulphur (H. ROSE [§]). [According to SOUCHAY,[‖] sulphide of lead is obtained pure by ignition with excess of sulphur in hydrogen, if only the lower one-fourth of the crucible be heated to redness for 5–10 minutes. The results were rather too low than too high.] It dissolves in concentrated hot hydrochloric acid, with evolution of sulphuretted hydrogen. In moderately strong nitric acid, sulphide of lead dissolves, upon the application of heat, with separation of sulphur;—if the acid is rather concentrated, a small portion of sulphate of lead is also formed. Fuming nitric acid acts energetically upon sulphide of lead, and converts it into sulphate without separation of sulphur.

Pb	103·50	86·61
S	16·00	13·39
	119·50	100·00

f. For the composition and properties of *chromate of lead*, see *chromic acid*, § 93, 2.

§ 84.

3. SUBOXIDE OF MERCURY; and 4. OXIDE OF MERCURY.

Mercury is weighed either in the METALLIC state, as SUBCHLORIDE, or as SULPHIDE, or occasionally also as OXIDE.

a. Metallic mercury, when pure, presents a perfectly bright surface.

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[*] Journ. f. prakt. Chem. 62, 381.

[†] Journ. f. prakt. Chem. 67, 374.

[‡] Pogg. Annal. 91, 110; and 110, 134.

[§] Pogg. Annal. 110, 135.

[‖] [Fres. Zeitschrift, IV. 65.]

It is unalterable in the air at the common temperature. It boils at 360°. It evaporates, but very slowly, at summer temperatures. Upon long-continued boiling with water, a small portion of mercury volatilizes, and traces escape along with the aqueous vapor, whilst a very minute proportion remains suspended (not dissolved) in the water (comp. Expt. No. 54). This suspended portion of mercury subsides completely after long standing. When metallic mercury is precipitated from a fluid, in a very minutely divided state, the small globules will readily unite into a large one if the mercury be perfectly pure; but even the slightest trace of extraneous matter, such as fat, &c., adhering to the mercury will prevent the union of the globules. Mercury does not dissolve in hydrochloric acid, not even in concentrated; it is barely soluble in dilute cold sulphuric acid, but dissolves readily in nitric acid, and in boiling concentrated sulphuric acid.

b. Subchloride of mercury, prepared in the wet way, is a heavy white powder. It is almost absolutely insoluble in cold water; in boiling water it is gradually decomposed, the water taking up chlorine and mercury; upon continued boiling, the residue acquires a gray color. Highly dilute hydrochloric acid fails to dissolve subchloride of mercury at the common temperature, but dissolves it slowly at a higher temperature; upon ebullition, with access of air, the whole of the subchloride is gradually dissolved by the dilute acid: the solution contains chloride of mercury ($Hg_2\,Cl + H\,Cl + O = 2\,Hg\,Cl + H\,O$). Subchloride of mercury, when acted upon by boiling concentrated hydrochloric acid, is rather speedily decomposed into mercury, which remains undissolved, and chloride of mercury, which dissolves. Boiling nitric acid dissolves subchloride of mercury, and converts it into chloride and nitrate of mercury. Chlorine water and nitrohydrochloric acid dissolve it to chloride, even in the cold. Solutions of alkaline chlorides decompose subchloride of mercury into metallic mercury and chloride of mercury, which latter dissolves; at a low temperature, this decomposition is confined to a small portion of the subchloride, but the application of heat promotes the decomposing action of these solutions. Subchloride of mercury does not affect vegetable colors; it is unalterable in the air, and may be dried at 100°, without suffering any diminution of weight; when exposed to a higher degree of heat, though still below redness, it volatilizes completely, without previous fusion.

Hg_2	200·00	84·94
Cl	35·46	15·06
	235·46	100·00

c. Sulphide of mercury, prepared in the wet way, is a black powder, insoluble in water. Dilute hydrochloric and dilute nitric acid fail to dissolve it, and it remains insoluble even in boiling hydrochloric acid; it is only very slightly soluble in hot concentrated nitric acid, but it dissolves readily in nitrohydrochloric acid. From a solution of chloride of mercury, containing much free hydrochloric acid, the whole of the metal cannot be precipitated by means of sulphuretted hydrogen, as $Hg\,S$, until the solution is properly diluted. Should such a solution be very concentrated, subchloride of mercury and sulphur are precipitated (M. MARTIN *). Solution of potassa, even boiling, fails to dissolve it. It dissolves in sulphide of potassium, but readily only in presence of free alkali (Expt. No. 55). Sulphide of ammonium, cyanide of potassium, and sulphite of soda do not dissolve it. On account of the solubility of sulphide of mercury in sulphide of potassium, it is impossible to precipitate mercury by means of sulphide of ammonium completely from solutions containing hydrate or carbonate of potassa or soda. In the air it is unalterable, even in the moist state, and at 100°. When exposed to a higher temperature, it sublimes completely and unaltered.

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* Journ. f. prakt. Chem. 67, 376.

Hg	100·00	86·21
S	16·00	13·79
	116·00	100·00

d. Oxide of mercury, prepared in the dry way, is a crystalline brick-colored powder, which, when exposed to the action of heat, changes to the color of cinnabar, and subsequently to a violet-black tint. It bears a tolerably strong heat without suffering decomposition; but, when heated to incipient redness, it is decomposed into mercury and oxygen; perfectly pure oxide of mercury leaves no residue upon continued exposure to a red heat. The escaping fumes also should not redden litmus paper. Water takes up a trace of oxide of mercury, acquiring thereby a very weak alkaline reaction. Hydrochloric or nitric acid dissolves it readily.

Hg	100·00	92·59
O	8·00	7·41
	108·00	100·00

§ 85.

5. OXIDE OF COPPER.

Copper is usually weighed in the METALLIC STATE, or in the form of OXIDE, or of SUBSULPHIDE. Besides these forms, we have to examine the SULPHIDE, the SUBOXIDE, and the SUBSULPHOCYANIDE.

a. Copper fuses only at a white heat. Exposure to dry air, or to moist air, free from carbonic acid, leaves the fused metal unaltered; but upon exposure to moist air impregnated with carbonic acid, it becomes gradually tarnished and coated with a film, first of a blackish-gray, finally of a bluish-green color. Precipitated finely divided copper, in contact with water and air, oxidizes far more quickly, especially at an elevated temperature. On igniting copper in the air, a layer of black oxide forms on its surface. Hydrochloric acid fails to dissolve it, even upon boiling, if the air is excluded; but with free access of air it dissolves it slowly. Copper dissolves readily in nitric acid. In ammonia it dissolves slowly if free access is given to the air; but it remains insoluble in that menstruum if the air is excluded. Metallic copper brought into contact in a closed vessel with solution of chloride of copper in hydrochloric acid, or with an ammoniacal solution of oxide of copper, reduces the chloride to subchloride, or the oxide to suboxide, an equivalent of metal being dissolved for every equivalent of chloride or oxide.

b. Oxide of copper.—If a dilute, cold, aqueous solution of a salt of oxide of copper is mixed with solution of potassa or soda in excess, a light blue precipitate of hydrated oxide of copper (CuO, HO) is formed, which is difficult to wash. If the precipitate be left in the fluid from which it has been precipitated, it will gradually become brownish black, and pass into $3CuO, HO$ (Harms[*]).

This transformation is immediate upon heating the fluid nearly to boiling. The fluid filtered off from the black precipitate is free from copper. If the solutions in question are mixed in a concentrated state, in addition to the formation of the blue precipitate, the fluid itself acquires a blue color, owing to a portion of very minutely divided hydrated oxide remaining suspended in it. From a fluid of this description protracted boiling will fail to precipitate all the copper; after dilution with water, the object is readily attained. If a solution of a salt of copper contains non-volatile organic substances, the addition of alkali in excess will, even upon boiling, fail to precipitate the whole of the copper as oxide. The hydrate ($3CuO, HO$) precipitated with potassa or soda from hot dilute solutions may be completely freed from the precipitant by washing with boiling water. Oxide of copper, prepared by igniting the hydrate or carbonate or nitrate of copper, is a brownish-black, or black powder, which remains unaltered upon strong ignition over the gas- or spirit-lamp, provided all reducing gases be excluded (Expt. No. 59). It is very readily reduced by ignition with charcoal, or reducing gases; heated in the air, the reduced copper re-oxidizes. Mixed with sulphur and ignited in a current of hydrogen, towards the end strongly, the oxide of copper passes into subsulphide (Cu_2S; H. Rose). Oxide of copper, in contact with the atmosphere, absorbs water; oxide that has been but slightly ignited absorbs the water more rapidly than such as has been strongly ignited (Expt. No. 57). Oxide of copper is nearly insoluble in water; but it dissolves readily in hydrochloric acid, nitric acid, &c.; less readily in ammonia. It does not affect vegetable colors.

Cu	31·70	79·85
O	8·00	20·15
	39·70	100·00

c. Sulphide of copper, prepared in the wet way, is a brownish-black, or black precipitate, almost absolutely insoluble in water;[†] when the recently prepared precipitate, in a moist state, is exposed to the air, it acquires a greenish tint and the property of reddening litmus paper, sulphate of copper being formed. Hence it must be washed with water containing sulphuretted hydrogen. [When digested near the boiling point for many hours, with addition of sulphuretted hydrogen if needful, it is permanent in air, and may be washed with hot water without danger of oxidation.] Sulphide of copper dissolves readily in boiling nitric acid, with separation of sulphur. Hydrochloric acid dissolves it with difficulty. This is the reason why sulphuretted hydrogen precipitates copper entirely from solutions which contain even a very large amount of free hydrochloric acid (Grundmann[‡]). Only when we dissolve a copper salt straight in pure hydrochloric acid of 1·1 sp. gr. does any copper remain unprecipitated (M. MARTIN*). It does not dissolve in solutions of potassa and of sulphide of potassium, particularly if these solutions be boiling; but it dissolves perceptibly in sulphide of ammonium, and readily in cyanide of potassium. Upon intense ignition in a current of hydrogen gas it is converted into pure $Cu_2\,S$.

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[*] Arch. der Pharm. 139, 35.

[†] In some experiments that I made when examining the Weilbach water I found that about 950000 parts of water are required to dissolve 1 part of CuS.

[‡] Journ. f. prakt. Chem 73, 241.

d. Suboxide of copper.—If the blue solution which is obtained upon adding to solution of oxide of copper tartaric acid and then solution of soda in excess, is mixed with solution of grape sugar or sugar of milk, and heat applied, an orange-yellow precipitate of hydrated suboxide of copper is formed, which contains the whole of the copper originally present in the solution, and after a short time, more particularly upon the application of a somewhat strong heat, turns red, owing to the conversion of the hydrate into anhydrous suboxide ($Cu_2\,O$). The precipitate, which is insoluble in water, retains a portion of alkali with considerable tenacity. When acted upon with dilute sulphuric acid, it gives sulphate of copper, which dissolves, and metallic copper, which separates.

e. Subsulphocyanide of copper (Cu_2, $Cy\,S_2$), formed when sulphocyanide of potassium is added to a solution of oxide of copper, mixed with sulphurous or hypophosphorous acid, is a white precipitate insoluble in water, and in dilute hydrochloric or sulphuric acid. On drying the salt retains water, and is, therefore, not adapted for direct weighing. When mixed with sulphur and ignited in hydrogen, it yields $Cu_2\,S$.

f. Subsulphide of copper separates from hot dilute acid solutions on addition of hyposulphite of soda, as a black precipitate that may be washed without risk of oxidation. When produced by heating Cu S in a current of hydrogen gas, or Cu_2, $Cy\,S_2$, with sulphur, it is a grayish-black mass, which may be ignited and fused, without suffering decomposition, if the air is excluded.

Cu_2	63·40	79·85
S	16·00	20·15
	79·40	100·00

§ 86.

6. TEROXIDE OF BISMUTH.

Bismuth is weighed in the form of TEROXIDE or as CHROMATE ($Bi\,O_3$, $2\,Cr\,O_3$). Besides these compounds, we have to study here the BASIC CARBONATE, the BASIC NITRATE, and the TERSULPHIDE.

a. Teroxide of bismuth, prepared by igniting the carbonate or nitrate, is a pale lemon-yellow powder which, under the influence of heat, assumes transiently a dark yellow or reddish-brown color. When heated to intense redness, it fuses, without alteration of weight. Ignition with charcoal, or in a current of carbonic oxide gas, reduces it to the metallic state. Fusion with cyanide of potassium also effects its complete reduction to the metallic state (H. ROSE †). It is insoluble in water, and does not affect vegetable colors. It dissolves readily in those acids which form soluble salts with it. When ignited with chloride of ammonium it gives metallic bismuth, the reduction being attended with deflagration.

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* Journ. f. prakt. Chem. 67, 375.

† Ibid. 61, 188

Bi	208	89·655
O_3	24	10·345
	232	100·000

b. Carbonate of bismuth.—Upon adding carbonate of ammonia in excess to a solution of bismuth, free from hydrochloric acid, a white precipitate of carbonate of bismuth ($Bi\,O_3$, $C\,O_2$) is immediately formed; part of this precipitate, however, redissolves in the excess of the precipitant. But if the fluid with the precipitate be heated before filtration, the filtrate will be free from bismuth. (Carbonate of potassa likewise precipitates solutions of bismuth completely; but the precipitate in this case invariably contains traces of potassa, which it is very difficult to remove by washing. Carbonate of soda precipitates solutions of bismuth less completely than the carbonates of ammonia and potassa.) The precipitate obtained by means of carbonate of ammonia, is easily washed; it is very nearly insoluble in water, but dissolves readily, with effervescence, in hydrochloric acid and nitric acid. Upon ignition it loses its carbonic acid, leaving teroxide of bismuth.

c. The *basic nitrate of bismuth*, which is obtained by mixing with water a solution of the nitrate containing little or no free acid, presents the appearance of a white, crystalline powder. It cannot be washed with pure cold water, without suffering a decided alteration. It becomes more basic, while the washings show an acid reaction, and contain bismuth. If the basic salt, however, be washed with cold water containing $\frac{1}{500}$ of nitrate of ammonia, no bismuth passes through the filter. The solution of nitrate of ammonia must not be warm. These remarks only apply in the absence of free nitric acid (J. Löwe*). On ignition the basic nitrate passes into the pure teroxide.

d. Chromate of bismuth ($Bi\,O_3$, $2\,Cr\,O_3$), which is produced by adding bichromate of potassa, slightly in excess, to a neutral solution of nitrate of bismuth, is an orange-yellow, dense, readily-subsiding precipitate, insoluble in water, even in presence of some free chromic acid, but soluble in hydrochloric acid and nitric acid. It may be dried at from 100° to 112°, without suffering decomposition (Löwe †).

$Bi\,O_3$	232·00	69·78
$2\,Cr\,O_3$	100·48	30·22
	332·48	100·00

e. Tersulphide of bismuth, prepared in the wet way, is a brownish-black, or black precipitate, insoluble in water, dilute acids, alkalies, alkaline sulphides, sulphite of soda, and cyanide of potassium. In moderately concentrated nitric acid it dissolves, especially on warming, to nitrate, with separation of sulphur. Hence in precipitating bismuth from a nitric acid solution, care should be taken to dilute sufficiently. Hydrochloric acid impedes the precipitation of bismuth by sulphuretted hydrogen only when a very large excess is present, and the fluid is quite concentrated. The sulphide does not change in the air. Dried at 100°, it continually takes up oxygen and increases slightly in weight; if the drying is protracted this increase may be considerable (Expt. No. 58). Fused with cyanide of potassium, it is completely reduced (H. Rose). Reduction takes place more slowly by ignition in a current of hydrogen.

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* Journ. f. prakt. Chem. 74, 341.

† Ibid. 67, 291.

Bi	208	81·25
S_3	48	18·75
	256	100·00

§ 87.

7. Oxide of Cadmium.

Cadmium is weighed either as oxide or as sulphide. Besides these substances, we have to examine carbonate of cadmium.

a. Oxide of cadmium, produced by igniting the carbonate or nitrate of cadmium, is a powder, the color of which varies from yellowish brown to reddish brown. The application of a white heat fails to fuse, volatilize, or decompose it; it is insoluble in water, but dissolves readily in acids; it does not alter vegetable colors. Ignition with charcoal, or in a current of hydrogen, carbonic oxide, or carburetted hydrogen, reduces it readily, the metallic cadmium escaping in the form of vapor.

Cd	56·00	87·50
O	8·00	12·50
	64·00	100·00

b. Carbonate of cadmium is a white precipitate, insoluble in water and in the fixed alkaline carbonates, and extremely sparingly soluble in carbonate of ammonia. It loses its water completely upon desiccation. Ignition converts it into oxide.

c. Sulphide of cadmium, produced in the wet way, is a lemon-yellow to orange-yellow precipitate, insoluble in water, dilute acids, alkalies, alkaline sulphides, sulphite of soda, and cyanide of potassium (Expt. No. 59). It dissolves readily in concentrated hydrochloric acid, with evolution of sulphuretted hydrogen. In precipitating, therefore, with sulphuretted hydrogen, a cadmium solution should not contain too much hydrochloric acid, and should be sufficiently diluted. The sulphide dissolves in moderately concentrated nitric acid, with separation of sulphur. It may be washed, and dried at 100° or 105°, without undergoing decomposition. Even on gently igniting the sulphide of cadmium in a current of hydrogen, it volatilizes in appreciable amount (H. Rose*), partially unchanged, partially as metallic vapor.

Cd	56·00	77·78
S	16·00	22·22
	72·00	100·00

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* Pogg. Annal. 110, 134.

METALLIC OXIDES OF THE SIXTH GROUP.

§ 88.

1. TEROXIDE OF GOLD.

Gold is always weighed in the metallic state. Besides METALLIC GOLD, we have to consider the TERSULPHIDE.

a. Metallic gold, obtained by precipitation, presents the appearance of a blackish-brown powder, destitute of metallic lustre, which it assumes, however, upon pressure or friction; when coherent in a compact mass, it exhibits the well-known bright yellow color peculiar to it. It fuses only at a white heat, and resists, accordingly, all attempts at fusion over a spirit-lamp. It remains wholly unaltered in the air and at a red heat, and is not in the slightest degree affected by water, nor by any simple acid. Nitrohydrochloric acid dissolves it to terchloride.

b. Tersulphide of gold.—When sulphuretted hydrogen is transmitted through a cold dilute solution of terchloride of gold, the whole of the gold separates as tersulphide ($Au\ S_3$), in form of a brownish-black precipitate. If this precipitate is left in the fluid, it is gradually transformed into metallic gold and free sulphuric acid. Upon transmitting sulphuretted hydrogen through a warm solution of terchloride of gold, a protosulphide ($Au\ S$) precipitates, with simultaneous formation of sulphuric and hydrochloric acids.

$$(2\ Au\ Cl_3 + 3\ H\ S + 3\ H\ O = 2\ Au\ S + 6\ H\ Cl + S\ O_3.)$$

The tersulphide is insoluble in water, hydrochloric acid, and nitric acid, but dissolves in nitrohydrochloric acid. The colorless sulphide of ammonium fails to dissolve it; but it dissolves almost entirely in the yellow sulphide of ammonium, and completely upon addition of potassa. It dissolves in potassa, with separation of gold. Yellow sulphide of potassium dissolves it completely. Exposure to a moderate heat reduces it to the metallic state.

§ 89.

2. BINOXIDE OF PLATINUM.

Platinum is invariably weighed in the METALLIC STATE; it is generally precipitated as BICHLORIDE OF PLATINUM AND CHLORIDE OF AMMONIUM, or as BICHLORIDE OF PLATINUM AND CHLORIDE OF POTASSIUM, rarely as BISULPHIDE OF PLATINUM.

a. Metallic platinum, produced by igniting the bichloride of platinum and chloride of ammonium, or the bichloride of platinum and chloride of potassium, presents the appearance of a gray, lustreless, porous mass (spongy platinum). The fusion of platinum can be effected only at the very highest degrees of heat. It remains wholly unaltered in the air, and even the most intense heat of our furnaces fails to affect it. It is not attacked by water, or simple acids, and scarcely by aqueous solutions of the alkalies. Nitrohydrochloric acid dissolves it to bichloride.

b. The properties of *bichloride of platinum and chloride of potassium*, and those of *bichloride of platinum and chloride of ammonium*, have been given already in §§ 68 and 70 respectively.

c. Bisulphide of platinum.—When a concentrated solution of bichloride of platinum is mixed with sulphuretted hydrogen water, or when sulphuretted hydrogen gas is transmitted through a rather dilute solution of the bichloride, no precipitate forms at first; after standing some time, however, the solution turns brown, and finally a precipitate subsides. But if the mixture of solution of bichloride of platinum with sulphuretted hydrogen in excess, is gradually heated (finally to ebullition), the whole of the platinum separates as bisulphide (free from any admixture of bichloride). The bisulphide of platinum is insoluble in water and in simple acids; but it dissolves in nitrohydrochloric acid. It dissolves partly in caustic alkalies, with separation of platinum, and completely in alkaline sulphides. When sulphuretted hydrogen is transmitted through water holding minutely divided bisulphide of platinum in suspension, the bisulphide, absorbing sulphuretted hydrogen, acquires a light grayish-brown color; the sulphuretted hydrogen thus absorbed, separates again upon exposure to the air. When moist bisulphide of platinum is exposed to the air, it is gradually decomposed, being converted into metallic platinum and sulphuric acid. Ignition in the air reduces bisulphide of platinum to the metallic state.

§ 90.

3. TEROXIDE OF ANTIMONY.

Antimony is weighed as TERSULPHIDE, as ANTIMONIOUS ACID, or more rarely in the METALLIC state.

a. Upon transmitting sulphuretted hydrogen through a solution of terchloride of antimony mixed with tartaric acid, an orange-red precipitate of *amorphous tersulphide* is obtained, mixed at first with a small portion of basic terchloride of antimony. However, if the fluid is thoroughly saturated with sulphuretted hydrogen, and a gentle heat applied, the terchloride mixed with the precipitate is decomposed, and the pure tersulphide of antimony obtained. Tersulphide of antimony is insoluble in water and dilute acids; it dissolves in concentrated hydrochloric acid, with evolution of sulphuretted hydrogen. In precipitating with sulphuretted hydrogen, therefore, antimony solutions should not contain too much free hydrochloric acid, and should be sufficiently diluted. The amorphous tersulphide dissolves readily in potassa, sulphide of ammonium, and sulphide of potassium, sparingly in ammonia, very slightly in carbonate of ammonia, and not at all in bisulphite of potassa. The amorphous sulphide, dried in the desiccator at the ordinary temperature, loses very little weight at 100°; if kept longer at this latter temperature, its weight remains constant. But it still retains a little water, which does not perfectly escape even at 190°, but at 200° the sulphide becomes anhydrous, turning black and crystalline (H. ROSE* and Expt. No. 60). Ignited gently in a stream of carbonic acid, the weight of this anhydrous sulphide remains constant; in a very intense heat, a small amount volatilizes. The amorphous sulphide, if long exposed to the action of air, in presence of water, slowly takes up oxygen, so that on treatment with tartaric acid it yields a filtrate containing teroxide.

The sulphides corresponding to the antimonious and antimonic acids are equally insoluble in water, also in water containing sulphuretted hydrogen. The pure pentasulphide dissolves completely in ammonia, especially on warming; traces only dissolve in carbonate of ammonia. On heating the dried pentasulphide in a current of carbonic acid 2 eq. of sulphur escape, black crystalline tersulphide remaining.

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* Journ. f. prakt. Chem. 59, 331.

On treating the ter- or penta-sulphide with fuming nitric acid violent oxidation sets in. We obtain first antimonic acid and pulverulent separated sulphur; on evaporating to dryness, antimonic acid and sulphuric acid; and lastly, on igniting, antimonious acid. The same (antimonious acid) is obtained by igniting the sulphide with 30 to 50 times its amount of oxide of mercury (Bunsen *). Ignition in a current of hydrogen converts the sulphides of antimony into the metallic state.

Sb	122·00	71·77
S_3	48·00	28·23
	170·00	100·00

b. Antimonious acid is a white powder, which, when heated, acquires transiently a yellow tint; it is infusible; it is fixed, provided reducing gases be excluded. It is almost insoluble in water, and dissolves in hydrochloric acid with very great difficulty. It undergoes no alteration on treatment with sulphide of ammonium. It manifests an acid reaction when placed upon moist litmus paper.

Sb	122·0	79·22
O_4	32·0	20·78
	154·0	100·00

c. Metallic antimony, produced in the wet way, by precipitation, presents the appearance of a lustreless black powder. It may be dried at 100° without suffering any alteration. It fuses at a moderate red heat. Upon ignition in a current of gas, *e.g.* hydrogen, it volatilizes, without formation of antimonetted hydrogen. Hydrochloric acid has very little action on it, even when concentrated and upon ebullition. Nitric acid converts it into teroxide of antimony, mixed with more or less antimonious acid, according to the concentration of the nitric acid.

§ 91.

4. PROTOXIDE OF TIN; and 5. BINOXIDE OF TIN.

Tin is generally weighed in the form of BINOXIDE; besides the binoxide, we have to examine PROTOSULPHIDE and BISULPHIDE OF TIN.

a. Binoxide of tin.—The hydrate of the binoxide *b* (*hydrated metastannic acid*) is obtained in the form of a white precipitate, by the action of nitric acid upon metallic tin, or by evaporating a solution of tin with nitric acid in excess. This precipitate is insoluble in water, nitric acid, and sulphuric acid, and dissolves but sparingly in hydrochloric acid. It reddens litmus, even when thoroughly washed. But if we precipitate solution of bichloride of tin with an alkali, or with sulphate of soda, or nitrate of ammonia, we obtain the hydrate of the binoxide *a*, which dissolves readily in hydrochloric acid. Upon intense ignition, both hydrates are converted into the anhydrous binoxide of tin. Mere heating to redness is not sufficient to expel all the water (Dumas †).

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* Annal. d. Chem. u. Pharm. 106, 3.

† Ibid. 105, 104.

Binoxide of tin is a straw-colored powder, which, under the influence of heat, transiently assumes a different tint, varying from bright yellow to brown. It is insoluble in water and acids, and does not alter the color of litmus paper. Mixed with chloride of ammonium in excess, and ignited, it volatilizes completely as bichloride. If binoxide of tin is fused with cyanide of potassium, all the tin is obtained in form of metallic globules, which may be completely, and without the least loss of metal, freed from the adhering slag, by extracting with dilute spirit of wine and rapidly decanting the fluid from the tin globules (H. Rose *).

Sn	59	78·67
O_2	16	21·33
	75	100·00

b. Hydrated protosulphide of tin forms a brown precipitate, insoluble in water, sulphuretted hydrogen water, and dilute acids. In precipitating tin from solutions of the protoxide by means of sulphuretted hydrogen, free hydrochloric acid must not be present in too large amount, and the solution must be diluted sufficiently. Ammonia fails to dissolve it; but it dissolves pretty readily (as bisulphide) in the yellow sulphide of ammonium, and in the yellow sulphide of potassium; it dissolves readily in hot concentrated hydrochloric acid. Heated, with exclusion of air, it loses its water of hydration, and is converted into anhydrous protosulphide of tin; when exposed to the continued action of a gentle heat, with free access of air, it is converted into sulphurous acid, which escapes, and binoxide of tin, which remains.

c. Hydrated bisulphide of tin forms a light-yellow precipitate. In washing with pure water, it is inclined to yield a turbid filtrate and to stop up the pores of the filter; this annoyance is got over by washing with water containing chloride of sodium, acetate of ammonia, or the like (Bunsen). On drying, the precipitate assumes a darker tint. It is insoluble in water; it dissolves with difficulty in ammonia, but readily in potassa, alkaline sulphides, and hot concentrated hydrochloric acid. It is insoluble in bisulphite of potassa. In precipitating tin from solutions of the binoxide by sulphuretted hydrogen, the solution should not contain too much free hydrochloric acid, and should be sufficiently diluted. When heated, with exclusion of air, it loses its water of hydration, and, at the same time, according to the greater or less degree of heat applied, one-half, or a whole equivalent of sulphur, becoming converted either into sesquisulphide, or into protosulphide of tin; when heated very slowly, with free access of air, it is converted into binoxide of tin, with disengagement of sulphurous acid.

§ 92.

6. Arsenious Acid; and 7. Arsenic Acid.

Arsenic is weighed either as ARSENIATE OF LEAD, as TERSULPHIDE, as ARSENIATE OF MAGNESIA AND AMMONIA, or as BASIC ARSENIATE OF SESQUIOXIDE OF IRON; besides these forms, we have here to examine also ARSENIO-MOLYBDATE OF AMMONIA.

a. Arseniate of lead, in the pure state, is a white powder, which agglutinates when exposed to a gentle red heat, at the same time transitorily acquiring a yellow tint; it fuses when exposed to a higher degree of heat. When strongly ignited, it suffers a slight diminution of weight, losing a small proportion of arsenic acid, which escapes as arsenious acid and oxygen. In analysis we have never occasion to operate upon the pure arseniate of lead, but upon a mixture of it with free oxide of lead.

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* Journ. f. prakt. Chem. 61, 189.

b. Tersulphide of arsenic forms a precipitate of a rich yellow color; it is insoluble in water,* and also in sulphuretted hydrogen water. When boiled with water, or left for several days in contact with that fluid, it undergoes a very trifling decomposition: a trace of arsenious acid dissolves in the water, and a minute proportion of sulphuretted hydrogen is disengaged. This does not in the least interfere, however, with the washing of the precipitate. The precipitate may be dried at 100°, without suffering decomposition; the whole of the water which it contains is expelled at that temperature. When exposed to a stronger heat, tersulphide of arsenic transitorily assumes a brownish-red color, fuses, and finally rises in vapor, without suffering decomposition. It dissolves readily in alkalies, alkaline carbonates, alkaline sulphides, bisulphite of potassa, and nitrohydrochloric acid; but it is scarcely soluble in boiling concentrated hydrochloric acid. Red fuming nitric acid converts it into arsenic acid and sulphuric acid.

As	75	60·98
S_3	48	39·02
	123	100·00

c. Arseniate of magnesia and ammonia forms a white, somewhat transparent, finely crystalline precipitate, which has the formula $2\ Mg\ O, N\ H_4\ O, As\ O_5 + 12\ aq.$

At 100°, it loses 11 eq. water; the formula of the precipitate dried at that temperature is accordingly $2\ Mg\ O, N\ H_4\ O, As\ O_5 + aq.$ Upon ignition it loses its water and ammonia, and changes to $2\ Mg\ O, As\ O_5$. But as the ammoniacal gas exercises a reducing action upon the arsenic acid, the new compound suffers a loss of weight, which is the more considerable the longer the ignition is continued; it amounts to from 4—12 per cent. of the arsenic originally present in the salt (H. ROSE). Arseniate of magnesia and ammonia dissolves very sparingly in water, one part of the salt dried at 100°, requiring 2656, one part of the anhydrous salt, 2788 parts of water of 15°. It is still more sparingly soluble in ammoniated water, one part of the salt dried at 100° requiring 15038, one part of the anhydrous salt, 15786 parts of a mixture of one part of solution of ammonia (0·96 sp. gr.), and 3 parts of water at 15°. In water containing chloride of ammonium, it is much more readily soluble, one part of the anhydrous salt requiring 886 parts of a solution of one part of chloride of ammonium in 7 parts of water. Presence of ammonia diminishes the solvent capacity of the chloride of ammonium solution: one part of the anhydrous salt requires 3014 parts of a mixture of 60 parts of water, 10 of solution of ammonia (0·96 sp. gr.) and one of chloride of ammonium.†

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* In some experiments which I had occasion to make, in the course of an analysis of the springs of Wielbach (Chemische Untersuchung der wichtigsten Mineralwasser des Herzogthums Nassau von Dr. Fresenius, V. Schwefelquelle zu Weilbach. Wiesbaden, Kreidel und Niedner. 1856), I found that one part of $As\ S_3$ dissolves in about 1 million parts of water.

† Zeitschrift f. anal. Chem. 3, 206.

COMPOSITION OF THE ARSENIATE OF MAGNESIA AND AMMONIA DRIED AT 100°.

$2\ Mg\ O$	40	21·05
$N\ H_4\ O$	26	13·68
$As\ O_5$	115	60·53
$H\ O$	9	4·74
	190	100·00

d. Arseniate of sesquioxide of iron.—The white slimy precipitate, produced by the action of ordinary arseniate of soda upon solution of sesquichloride of iron, has the composition $2\ Fe_2\ O_3,\ 3\ H\ O,\ 3\ As\ O_5 + 9$ aq. It dissolves in solution of ammonia, imparting a yellow color to the fluid.

Besides this compound, there exist still several others, with larger proportions of sesquioxide of iron; thus we have $Fe_2\ O_3,\ As\ O_5$, which falls down + 5 aq. upon the precipitation of arsenic acid with acetate of sesquioxide of iron (KOTSCHOUBEY); $2\ Fe_2\ O_3,\ As\ O_5$, which is obtained + 12 aq., when basic arseniate of protoxide of iron is oxidized with nitric acid, and ammonia added;—$16\ Fe_2\ O_3,\ As\ O_5$, which forms + 24 aq., upon boiling the less basic compounds with solution of potassa in excess; (BERZELIUS). The two latter compounds are not soluble in ammonia; the last is quite like hydrated sesquioxide of iron. [Doubtless the basic arseniate of sesquioxide of iron, like the analogous phosphate, loses acid as long as it is washed, and therefore the precipitate has no definite composition.] In BERTHIER's method of estimating arsenic acid, we obtain mixtures of these different salts. They are the better adapted for the purpose, the more basic they are; being the more insoluble in ammonia, and at the same time more easily washed. Upon ignition the water alone is expelled, provided the heat be very gradually increased. But if the salt is suddenly exposed to a strong heat, before the adhering ammonia has escaped, part of the arsenic acid is thereby reduced to arsenious acid (H. ROSE).

e. Arsenio-molybdate of ammonia.—If a fluid containing arsenic acid is mixed with a large proportion of molybdate of ammonia, and sufficient nitric or hydrochloric acid to redissolve the precipitate of molybdic acid which forms at first, and the fluid heated to boiling, a yellow precipitate of arsenio-molybdate of ammonia separates—provided the molybdic acid be present in excess. This precipitate comports itself with solvents like the analogous compound of phosphoric acid; it is, like the latter, insoluble in water, salts, and free acids, particularly nitric acid, provided an excess of solution of molybdate of ammonia, mixed with acid in moderate excess, be present. SELIGSOHN* found it to be composed of 87·666 per cent. of molybdic acid, 6·308 arsenic acid, 4·258 ammonia, and 1·768 water.

B.—FORMS IN WHICH THE ACIDS ARE WEIGHED OR PRECIPITATED.

ACIDS OF THE FIRST GROUP.

§ 93.

1. ARSENIOUS ACID and ARSENIC ACID.—See § 92.

2. CHROMIC ACID.

Chromic acid is weighed either in the form of SESQUIOXIDE, or in that of CHROMATE OF LEAD.

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* Journ. f. prakt. Chem. 67, 481.

a. Sesquioxide of chromium.—See § 76.

b. Chromate of lead obtained by precipitation forms a bright yellow precipitate, insoluble in water and acetic acid, barely soluble in dilute nitric acid, readily in solution of potassa. When chromate of lead is boiled with concentrated hydrochloric acid, it is readily decomposed, chloride of lead and sesquichloride of chromium being formed. Addition of alcohol tends to promote this decomposition. Chromate of lead is unalterable in the air; it dries thoroughly at 100°. Under the influence of heat it transitorily acquires a reddish-brown tint; it fuses at a red heat; when heated beyond its point of fusion, it loses oxygen, and is transformed into a mixture of sesquioxide of chromium and basic chromate of lead. Heated in contact with organic substances, it readily yields oxygen to the latter.

$Pb\,O$	111·50	68·94
$Cr\,O_3$	50·24	31·06
	161·74	100·00

3. Sulphuric Acid.

Sulphuric acid is determined best in the form of SULPHATE OF BARYTA, for the properties of which see § 71.

4. Phosphoric Acid.

The principal forms into which phosphoric acid is converted are as follows:—PHOSPHATE OF LEAD, PYROPHOSPHATE OF MAGNESIA, BASIC PHOSPHATE OF MAGNESIA ($3\,Mg\,O, P\,O_5$), BASIC PHOSPHATE OF SESQUIOXIDE OF IRON, PHOSPHATE OF SESQUIOXIDE OF URANIUM, PHOSPHATE OF BINOXIDE OF TIN, and PHOSPHATE OF SILVER. Besides these compounds, we have to examine PHOSPHATE OF SUBOXIDE OF MERCURY, and PHOSPHOMOLYBDATE OF AMMONIA.

a. The *phosphate of lead* obtained in the course of analysis is rarely quite pure, but is generally mixed with free oxide of lead. In this mixture we have accordingly the basic phosphate of lead ($3\,Pb\,O, P\,O_5$); in the pure state, this presents the appearance of a white powder; it is insoluble in water and in acetic acid, and equally so in ammonia; it dissolves readily in nitric acid. When exposed to the action of heat, it fuses, without undergoing decomposition.

b. Pyrophosphate of magnesia.—See § 74.

c. Basic phosphate of magnesia ($3\,Mg\,O, P\,O_5$).—This compound is produced by mixing a solution of an alkaline phosphate, containing chloride of ammonium, with magnesia, evaporating the mixture, heating the residue until the chloride of ammonium is completely expelled, and finally treating with water; the compound so produced contains an excess of magnesia. It is sufficient for our purpose to state that it is nearly absolutely insoluble in water and in solutions of salts of the alkalies (F. R. SCHULZE *).

d. Basic phosphate of sesquioxide of iron.

If a solution of phosphoric acid or of phosphate of lime in acetic acid is carefully precipitated with a solution of acetate of sesquioxide of iron, or with a mixture of iron-alum and acetate of soda, so that the iron salt may just predominate, the precipitate always contains 1 eq. $P\,O_5$ to 1 eq. $Fe_2\,O_3$ (RÄWSKY, WITTSTEIN, E. DAVY *); if, on the other hand, the acetate of iron is in larger excess, the precipitate contains more base. WITTSTEIN obtained, by using considerable excess of acetate of iron, a precipitate of the formula $4\,Fe_2\,O_3,\,3\,P\,O_5$. Precipitates, obtained with a small excess of the precipitant, possess a composition varying between the above-mentioned limits. RAMMELSBERG obtained $Fe_2\,O_3,\,P\,O_5$ (+ 4 aq.), and WITTSTEIN subsequently, the same compound (with 8 aq. instead of 4), upon mixing sulphate of sesquioxide of iron with phosphate of soda in excess; with an insufficient quantity of the phosphate of soda, the latter chemist obtained a more yellowish precipitate, which had the formula

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* Journ. f. prakt. Chem. 63, 440.

$$3\,(Fe_2O_3,\,P\,O_5+8\text{ aq.})+(Fe_2O_3,\,3\,H\,O).$$

If an acid fluid containing a *considerable* excess of phosphoric acid is mixed with a small quantity of solution of sesquioxide of iron, and an alkaline acetate added, a precipitate of the formula, $Fe_2O_3,\,P\,O_5$ + water, is invariably obtained, which, accordingly, leaves upon ignition $Fe_2\,O_3,\,P\,O_5$ (WITTSTEIN). Fresh experiments that I have made upon this subject have positively convinced me of the perfect correctness of this statement of WITTSTEIN's.†

COMPOSITION.

$P\,O_5$	71	47·02
Fe_2O_3	80	52·98
	151	100·00

[The discrepancies among the statements made by different chemists as to the composition of basic phosphate of sesquioxide of iron obtained in the modes above indicated are explained by the observations of MOHR, that the precipitate loses phosphoric acid as long as it is washed, and has consequently no definite composition.]

If we dissolve phosphate of sesquioxide of iron in hydrochloric acid, supersaturate the solution with ammonia, and apply heat, we obtain more basic salts, viz., $3\,Fe_2\,O_3,\,2\,P\,O_5$ (RAMMELSBERG); $2\,Fe_2\,O_3,\,P\,O_5$ (WITTSTEIN—after long washing). In WITTSTEIN's experiment, the wash-water contained phosphoric acid. The white phosphate of sesquioxide of iron does not dissolve in acetic acid, but it dissolves in a solution of acetate of sesquioxide of iron.

Upon boiling the latter solution (of phosphate of sesquioxide of iron in acetate of sesquioxide of iron), the whole of the phosphoric acid precipitates, together with the basic acetate of sesquioxide of iron, as *hyperbasic phosphate of sesquioxide of iron* ($15\,Fe_2O_3,\,PO_5$—(RAMMELSBERG). Similar extremely basic combinations are invariably obtained (often mixed with free hydrated sesquioxide of iron), upon precipitating with ammonia or carbonate of baryta a solution containing phosphoric acid and an excess of sesquioxide of iron. The precipitate obtained by carbonate of baryta, can be conveniently filtered off and washed, the filtrate is perfectly free from either iron or phosphoric acid; on the contrary, the precipitate obtained by ammonia, especially if the latter were much in excess, is slimy, and therefore difficult to wash, and the filtrate always contains small traces of both iron and phosphoric acid.

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* Phil. Mag., xix. p. 181. Journ. f. prakt. Chem. 80, 380.

† In an experiment made at a former period by Will and myself (Annal. der Chem. u. Pharm. 50, 379), we obtained in this way a precipitate of the formula $2\,Fe_2\,O_3,\,3\,P\,O_5+3\,HO+10$ aq.; but I have never since succeeded in producing a precipitate of the same composition.

e. Phosphate of sesquioxide of uranium.—If the hot aqueous solution of a phosphate soluble in water or acetic acid is mixed, in presence of free acetic acid, with acetate of sesquioxide of uranium, a precipitate of phosphate of sesquioxide of uranium is immediately formed. If the fluid contains much ammoniacal salt, the precipitate contains also ammonia. The same precipitate forms also if alumina or sesquioxide of iron is present; but in that case it is always mixed with more or less phosphate of sesquioxide of iron or phosphate of alumina. Presence of potassa- or soda-salts, on the contrary, or of salts of the alkaline earths, has no influence on the composition of the precipitate.

Phosphate of sesquioxide of uranium and ammonia ($2\,Ur_2\,O_3, N\,H_4\,O, P\,O_5 + x\,H\,O$) is a somewhat gelatinous, whitish-yellow precipitate, with a tinge of green. The best way of washing it, at least so far as the principal part of the operation is concerned, is by boiling with water and decanting. If, after having allowed the fluid in which the precipitate is suspended to cool a little, a few drops of chloroform are added, and the mixture is shaken or boiled up, the precipitate subsides much more readily than without this addition.

The precipitate is insoluble in water and in acetic acid; but it dissolves in mineral acids; acetate of ammonia, added in sufficient excess, completely re-precipitates it from this solution, upon application of heat. Upon igniting the precipitate, no matter whether containing ammonia or not, phosphate of sesquioxide of uranium of the formula $2\,Ur_2\,O_3, P\,O_5$ is produced. This has the color of the yolk of an egg. If the precipitate is ignited in presence of charcoal or of some reducing gas, partial reduction to phosphate of protoxide of uranium ensues, owing to which the ignited mass acquires a greenish tint; however, upon warming the greenish residue with some nitric acid, the green salt of the protoxide is readily reconverted into the yellow salt of the sesquioxide. Phosphate of sesquioxide of uranium is not hygroscopic, and may therefore be ignited and weighed in an open platinum dish (A. **Arendt** and W. **Knop** *).

$2\,Ur_2O_3$	285·6	80·09
$P\,O_5$	71·0	19·91
	356·6	100·00

The one-fifth part of the precipitate may accordingly be calculated as phosphoric acid in ordinary analyses.†

f. Phosphate of binoxide of tin is never obtained in the pure state in the analytical process, but contains always an admixture of hydrated metastannic acid in excess, which, upon ignition, changes to metastannic acid. It has, generally speaking, the same properties as hydrated metastannic acid, and is more particularly, like the latter, insoluble in nitric acid. Upon heating with concentrated solution of potassa, phosphate and metastannate of potassa are formed.

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* Chemisches Centralblatt, 1856, 769, 803; and 1857, 177.

† The equivalent of uranium is here taken as 59·4, according to Ebelmen. If we take it according to Peligot, as 60, the ignited phosphate would contain 80·22 $Ur_2\,O_3$, and 19·78 phosphoric acid. W. Knop and Arendt found in four experiments 20·13, 20·06, 20·04, and 20·04 respectively (in another 20·77). It will be seen that these numbers agree better with the composition as reckoned from Ebelmen's than from Peligot's equivalent.

g. Tribasic phosphate of silver is a yellow powder; it is insoluble in water, but readily soluble in nitric acid, and also in ammonia. In ammoniacal salts, it is difficultly soluble. It is unalterable in the air. Upon ignition, it acquires transiently a reddish-brown color; at an intense red heat, it fuses without decomposition.

$3\,AgO$	347·91	83·05
PO_5	71·00	16·95
	418·91	100·00

h. Phosphate of suboxide of mercury.—This compound is employed for the purpose of effecting the separation of phosphoric acid from many bases, after H. ROSE's method.

Phosphate of suboxide of mercury presents the appearance of a white crystalline mass, or of a white powder. It is insoluble in water, but dissolves in nitric acid. The action of a red heat converts it into fused phosphate of oxide of mercury, with evolution of vapor of mercury. Upon fusion with alkaline carbonates, alkaline phosphates are produced, and mercury, oxygen, and carbonic acid escape.

i. Phospho-molybdate of ammonia.—This compound also serves to effect the separation of phosphoric acid from other bodies; it is of the utmost importance in this respect.

Phospho-molybdate of ammonia forms a bright yellow, readily subsiding precipitate. Dried at 100°, it has, according to SELIGSOHN, the following (average) composition:—

Molybdic acid	90·744
Phosphoric acid	3·142
Oxide of ammonium	3·570
Water	2·544
	100·000 *

In the pure state, it dissolves but sparingly in cold water (1 in 10000—EGGERTZ); but it is soluble in hot water. It is readily soluble, even in the cold, in caustic alkalies, alkaline carbonates and phosphates, chloride of ammonium, and oxalate of ammonia. It dissolves only sparingly in sulphate of ammonia, nitrate of potassa, and chloride of potassium; and very sparingly in nitrate of ammonia.

It is soluble in sulphate of potassa and sulphate of soda, chloride of sodium and chloride of magnesium, and sulphuric, hydrochloric, and nitric acids (both concentrated and dilute). Water, containing 1 per cent. of common nitric acid, dissolves $\frac{1}{6600}$ (EGGERTZ). Application of heat does not check the solvent action of these substances. Presence of molybdate of ammonia totally changes its deportment with acid fluids: in presence of that substance, it is almost insoluble in acids, even upon ebullition. The solution of the phospho-molybdate of ammonia in acids is probably attended, in all cases, with decomposition and with separation of the molybdic acid, which cannot take place in the presence of molybdate of ammonia (J. CRAW *). Tartaric acid and similar organic substances entirely prevent the precipitation of the phospho-molybdate of ammonia (EGGERTZ).† In the presence of an iodide, instead of a yellow precipitate, a green precipitate or a green fluid is formed, resulting from the reducing action of the hydriodic acid on the molybdic acid (J. W. BILL ‡). Other substances which reduce molybdic acid have of course a similar action.

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* From the varying results of different analysts it is plain that the precipitate, prepared under apparently the same circumstances, has not always exactly the same composition. Sonnenschein (Journ. f. prakt. Chem. 53, 342) found in the precipitate dried at 120°, 2·93—3·12 % PO_5; Lipowitz (Pogg. Annal. 109, 135), in the precipitate dried at from 20 to 30°, 3·607 % PO_5; Eggertz (Journ. f. prakt. Chem. 79, 496), 3·7 to 3·8. [Dietrich (Fres. Zeitschrift für analyt. Chem. 1866, 45) says that this precipitate contains small and variable quantities of admixed molybdic acid. He finds, however, that the relation between PO_5 and NH_3 is constantly that of Seligsohn's formula $(23\,NH_4O\,PO_5) + 15\,(HO, 4\,MoO_3)$. Dietrich estimates PO_5 by bringing the ppt. into the azotometer.

5. BORACIC ACID.

BOROFLUORIDE OF POTASSIUM is the best form to convert boracic acid into for the purpose of the direct estimation of the acid. This compound is produced by mixing the solution of an alkaline borate (the potassa salt answers best) with hydrofluoric acid in excess, in a silver or platinum dish, and evaporating to dryness. The gelatinous precipitate which forms in the cold, dissolves upon application of heat, and separates from the solution subsequently, upon evaporation, in small, hard, transparent crystals. The compound has the formula $K\,Fl, B\,Fl_3$. It is soluble in water and also in dilute spirit of wine; but strong alcohol fails to dissolve it; it is insoluble also in concentrated solution of acetate of potassa. It may be dried at 100°, without suffering decomposition (AUG. STROMEYER§).

K	39·11	31·01
B	11·00	8·72
Fl	76·00	60·27
	126·11	100·00

6. OXALIC ACID.

When oxalic acid is to be directly determined it is usually precipitated in the form of OXALATE OF LIME; and its weight is inferred from the CARBONATE OF LIME produced from the oxalate by ignition. For the properties, &c., of carbonate of lime and of oxalate of lime, see § 73.

7. HYDROFLUORIC ACID.

The *direct* estimation of hydrofluoric acid is usually effected by weighing the acid in the form of FLUORIDE OF CALCIUM.

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* Chem. Gaz. 1852, 216.

† (Lipowitz (Jahresbericht, 1863, 618) recommends a molybdic solution containing tartaric acid for the precipitation of $P\,O_5$.

‡ Sillim. Journ., July, 1858. § Annal. d. Chem. u. Pharm. 100, 82.

Fluoride of calcium forms a gelatinous precipitate, which it is found difficult to wash. If digested with ammonia, previous to filtration, it is rendered denser and less gelatinous. It is not altogether insoluble in water; aqueous solutions of the alkalies fail to decompose it. It is very slightly soluble in dilute, but more readily in concentrated hydrochloric acid. When acted upon by sulphuric acid, it is decomposed, and sulphate of lime and hydrofluoric acid are formed. Fluoride of calcium is unalterable in the air, and at a red heat. Exposed to a very intense heat, it fuses. Upon intense ignition in moist air, it is slowly and partially decomposed into lime and hydrofluoric acid. Mixed with chloride of ammonium, and exposed to a red heat, fluoride of calcium suffers a continual loss of weight; but the decomposition is incomplete.

Ca	20	51·28
Fl	19	48·72
	39	100·00

8. Carbonic Acid.

The *direct* estimation of carbonic acid—which, however, is only rarely resorted to—is usually effected by weighing the acid in the form of CARBONATE OF LIME. For the properties of the latter substance, see § 73.

9. Silicic Acid (or Silica).

By whatever decomposition silicic acid is separated in the wet way, it is always hydrated. The hydrate is generally gelatinous, occasionally pulverulent. The amount of water it contains varies according to the circumstances under which it was formed; at least this is the only explanation I can give of the great differences in the results obtained by various chemists who have analyzed hydrates of silicic acid dried in the same way.*

The gelatinous hydrate of silicic acid is never entirely insoluble in water and acids. While however the degree of solubility is relatively high, if the hydrate immediately on separation comes in contact with large quantities of fluid, it is, on the contrary, low, when, after having been separated and washed, it is treated with solvents; thus 1 part of silicic acid in the hydrated condition, obtained by passing fluosilicic gas into water and washing the precipitate completely, requires 7700 parts of water, 11000 parts of cold, and 5500 parts of boiling hydrochloric acid of 1·115 sp. gr. (J. Fuchs, *loc. cit.*) Hydrate of silicic acid dried at 100° forms a loose, white powder; it is insoluble in water and in acids (hydrofluoric excepted), but it dissolves in solutions of the fixed alkalies and their carbonates, especially in the heat. The silicic acid is obtained in the same form, when its solution in water or in hydrochloric acid is evaporated and the residue dried at 100°.

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* Doveri (Annal. de Chim. et de Phys. 21, 40; Annal. d. Chem. u. Pharm. 64, 256) found in the air-dried hydrate 16·9 to 17·8 % water; J. Fuchs (Annal. d. Chem. u. Pharm. 82, 119 to 123), 9·1 to 9·6; G. Lippert (Expt No. 61), 9·28 to 9·95. Doveri found in the hydrate dried at 100°, 8·3 to 9·4; J. Fuchs, 6·63 to 6·96; G. Lippert, 4·97 to 5·52; H. Rose (Pogg. Annal. 108, 1; Journ. für prakt. Chem. 81, 227) found in the hydrate obtained by digesting stilbite with concentrated hydrochloric acid, and dried at 150°, 4·85 % water.

On ignition all the hydrates pass into the anhydrous acid. As the vapor escapes small particles of the extremely fine powder are liable to whirl up. This may be avoided by moistening the hydrate in the crucible with water, evaporating to dryness on a water bath, and then applying at first a slight and then a gradually increased heat.

The silicic acid obtained by igniting the hydrate appears in the amorphous condition, with a sp. gr. of 2·2 to 2·3. It forms a white powder insoluble in water and acids (hydrofluoric excepted), soluble in solutions of the fixed alkalies and their carbonates, especially in the heat. Hydrofluoric acid readily dissolves amorphous silicic acid; the solution leaves no residue on evaporation in platinum, if the silica was pure. The amorphous silica, when heated with fluoride of ammonium in a platinum crucible, readily volatilizes. The ignited amorphous silica, exposed to the air, eagerly absorbs water, which it will not give up at from 100 to 150°. (H. Rose.) Silica fuses at the strongest heat. The mass obtained is vitreous and amorphous.

Amorphous silica ignited with chloride of ammonium, at first loses weight, and then, when the ignition has rendered it denser, the weight remains constant.

The amorphous silica must be distinguished from the crystallized or crystalline variety, which occurs as rock crystal, quartz, sand, &c. This has a sp. gr. of 2·6 (Schaffgotsch), and is far more difficultly, and in far less amount, dissolved by potash solution or solution of fixed alkaline carbonates; it is also more slowly attacked by hydrofluoric acid or fluoride of ammonium.

Vegetable colors are not changed either by silicic acid or its hydrates.

Si	14·00	46·67
O_2	16·00	53·33
	30·00	100·00

ACIDS OF THE SECOND GROUP.

§ 94.

1. Hydrochloric Acid.

Hydrochloric acid is almost invariably weighed in the form of CHLORIDE OF SILVER—for the properties of which, see § 82.

2. Hydrobromic Acid.

Hydrobromic acid is always weighed in the form of BROMIDE OF SILVER.

Bromide of silver, prepared in the humid way, forms a yellowish-white precipitate. It is wholly insoluble in water and in nitric acid, tolerably soluble in ammonia, readily soluble in hyposulphite of soda and in cyanide of potassium. Concentrated solutions of the chlorides and bromides of potassium, sodium, and ammonium dissolve it to a very perceptible amount, while in very dilute solutions of these salts it is entirely insoluble. Traces only dissolve in nitrates of the alkalies. On digestion with excess of iodide of potassium solution it is completely converted into iodide of silver (Field). On ignition in a current of chlorine the bromide of silver is transformed into the chloride; on ignition in a current of hydrogen it is converted into metallic silver. Exposed to the light it gradually turns gray, and finally black. Under the influence of heat, it fuses to a reddish liquid, which, upon cooling, solidifies to a yellow horn-like mass. Brought into contact with zinc and water, bromide of silver is decomposed: a spongy mass of metallic silver forms, and the solution contains bromide of zinc.

Ag	107·97	57·44
Br	80·00	42·56
	187·97	100·00

3. Hydriodic Acid.

Hydriodic acid is usually determined in the form of iodide of silver, and occasionally also in that of protiodide of palladium.

a. Iodide of silver, produced in the humid way, forms a light-yellow precipitate, insoluble in water and in dilute nitric acid, and very slightly soluble in ammonia. One part dissolves, according to Wallace and Lamont,[*] in 2493 parts of aqueous ammonia sp. gr. 0·89, according to Martini, in 2510 parts, of 0·96 sp. gr. It is copiously taken up by concentrated solution of iodide of potassium, but it is insoluble in very dilute; it dissolves readily in hyposulphite of soda and in cyanide of potassium; traces only are dissolved by alkaline nitrates. Hot concentrated nitric and sulphuric acids convert it, but with some difficulty, into nitrate and sulphate of silver respectively, with expulsion of the iodine. Iodide of silver acquires a black color when exposed to the light. When heated, it fuses without decomposition to a reddish fluid, which, upon cooling, solidifies to a yellow mass, that may be cut with a knife. Under the influence of excess of chlorine in the heat it is completely converted into chloride of silver; ignition in hydrogen reduces it to the metallic state. When brought into contact with zinc and water, it is decomposed: iodide of zinc is formed, and metallic silver separates.

Ag	107·97	45·95
I	127·00	54·05
	234·97	100·00

b. Protiodide of palladium, produced by mixing an alkaline iodide with protochloride of palladium, is a deep brownish-black, flocculent precipitate, insoluble in water and in dilute hydrochloric acid, but slightly soluble in saline solutions (chloride of sodium, chloride of magnesium, chloride of calcium, &c.). It is unalterable in the air. Dried simply in the air, it retains one equivalent of water = 5·05 per cent. Dried long *in vacuo*, or at a rather high temperature (70° to 80°), it yields the whole of this water, without the least loss of iodine. Dried at 100°, it loses a trace of iodine; at from 300 to 400°, the whole of the iodine is expelled. The precipitated iodide of palladium may be washed with hot water, without loss of iodine.

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[*] Chem. Gaz. 1859, 137.

Pd	53·00	29·44
I	127·00	70·56
	180·00	100·00

4. Hydrocyanic Acid.

Hydrocyanic acid, if determined gravimetrically and directly, is always converted into CYANIDE OF SILVER—for the properties of which compound see § 82.

5. Hydrosulphuric Acid (or Sulphuretted Hydrogen).

The forms into which sulphuretted hydrogen, or the sulphur in metallic sulphides, is converted for the purpose of being weighed, are TERSULPHIDE OF ARSENIC, SULPHIDE OF SILVER, SULPHIDE OF COPPER, and SULPHATE OF BARYTA.

For the properties of the sulphides named, see §§ 82, 85, 92; for those of sulphate of baryta, see § 71.

ACIDS OF THE THIRD GROUP.

§ 95.

1. Nitric Acid; and 2. Chloric Acid.

These two acids are never estimated in a *direct* way—that is to say, in compounds containing them, but always in an *indirect* way; generally volumetrically.

SECTION IV.

THE DETERMINATION (OR ESTIMATION) OF BODIES.

§ 96.

In the preceding Section we have examined the composition and properties of the various forms and combinations in which bodies are separated from others, or in which they are weighed. We have now to consider the special means and methods of converting the several bodies into such forms and combinations.

For the sake of greater clearness and simplicity, we shall, in the present Section, confine our attention to the various methods applied to effect the *estimation of single bodies*, deferring to the next Section the consideration of the means adopted for the estimation of mixed bodies, or the *separation of bodies from one another*.

We have to deal here exclusively with bodies in the free state, or with compounds consisting of *one base and one acid*, or of *one metal and one metalloid*.

As in the "Qualitative Analysis," the acids of arsenic will be treated of among the bases, on account of their behavior to sulphuretted hydrogen, and those elements which form acids with hydrogen will be considered in conjunction with their respective hydrogen acids.

In the quantitative analysis of a body we have to study first, the most appropriate method of dissolving it; and, secondly, the modes of determining it.

With regard to the latter point, we have to turn our attention, first, to the *performance;* and secondly, to the *accuracy* of the methods.

It happens very rarely in quantitative analyses that the amount of a substance, as determined by the analytical process, corresponds exactly with the amount theoretically calculated or actually present; and if it does happen, it is merely by chance.

It is of importance to inquire what is the reason of this fact, and what are the limits of inaccuracy in the several methods.

The cause of this almost invariably occurring discrepancy between the quantity present and that actually found, is to be ascribed either exclusively to *the execution*, or it lies partly in the *method itself*.

The *execution* of the analytical processes and operations can never be *absolutely* accurate, even though the greatest care and attention be bestowed on the most trifling minutiæ. To account for this, we need only bear in mind that our weights and measures are never *absolutely* correct, nor our balances *absolutely* accurate, nor our reagents *absolutely* pure; and, moreover, that we do not weigh *in vacuo;* and that, even if we deduce the weight *in vacuo* from the weight we *actually* obtain by weighing in the air, the very volumes on which the calculation is based are but approximately known;—that the hygroscopic state of the air is [illegible] weighing of the empty crucible and of the [illegible] that we know the weight of a filter ash [illegible] never succeed in *completely* keeping

[illegible] many of them are not entirely free from [illegible];—precipitates are not *absolutely* in- [illegible] require ignition are not *absolutely* fixed; [illegible] have a slight tendency to volatilize; the [illegible] analyses is usually produced only by a small [illegible] which is occasionally liable to vary with the [illegible] rature, &c.

[illegible] can be pronounced quite free from defect; [illegible] for example, that even *sulphate of baryta* is [illegible] water. Whenever we describe any method as [illegible], we mean, that no causes of considerable in- [illegible]

[illegible] our analytical processes, invariably to contend [illegible] inaccuracy which it is impossible to overcome [illegible] operations be conducted with the most scru- [illegible] utmost attention to established rules. It will [illegible] that several defects and sources of error may, in [illegible] vitiate the results; whereas, in other cases, they [illegible] her, and thus enable us to attain a higher degree [illegible] *ative* accuracy of the results attainable by an [illegible] ates between two points—these points are called [illegible] the case of methods free from sources of error, [illegible] approach each other; thus, for instance, in the [illegible], with great care one will always be able to obtain [illegible] for the 100 parts of chlorine actually present.

[illegible] will, of course, exhibit far greater discrepan- [illegible] ation of strontia by means of sulphuric acid, the [illegible] skilful operator may not be able to obtain more than [illegible] for the 100 parts of strontia actually present. I [illegible] state that the numbers occasionally given in this [illegible] of the present work, to denote the degree of accu- [illegible] ds, refer invariably to the substance estimated [illegible] baryta, for instance), and not to the combination in [illegible] may be weighed (chloride of silver, bichloride of [illegible] of ammonium, sulphate of baryta, for instance); [illegible] of various methods would not be comparable.

[illegible] ainment of results *exactly* corresponding with the [illegible] does not always justify the assumption, on the part [illegible] his operations, to have led to such a result, must [illegible] with the utmost precision and accuracy. It may [illegible] in the course of the analytical process, that one error [illegible] another; thus, for instance, the analyst may, at the [illegible] of his operations, spill a minute portion of the substance [illegible]; whilst, at a later stage of the process, he may recover [illegible] imperfect washing of the precipitate. As a general rule, [illegible] a trifling deficiency of substance may be looked upon as [illegible] of accurate performance of the analytical process than [illegible] exhibiting an excess of substance.

[illegible] not the least effective means of guarding against error and inaccuracies in *gravimetric analyses*, I would most strongly recommend the analyst, *after weighing a precipitate, &c., to compare its properties (color, solubility, reaction, &c.) with those which it should possess*, and which have been amply described in the preceding Section.

In my own laboratory, I insist upon all substances that are weighed in the course of an analysis being kept between watch-glasses, until the whole affair is concluded. This affords always a chance of testing them once more for some impurity, the presence of which may become suspected in the after-course of the process.

I. ESTIMATION OF BASES IN COMPOUNDS CONTAINING ONLY ONE BASE AND ONE ACID, OR ONE METAL AND ONE METALLOID.

FIRST GROUP.

POTASSA—SODA—AMMONIA—(LITHIA).

§ 97.

1. Potassa.

a. Solution.

Potassa and its salts, with those inorganic acids which we have to consider here, are dissolved in water, in which menstruum they dissolve readily, or at all events, pretty readily.

Potassa salts with organic acids it is most convenient to convert into sulphate of potassa. See p. 152.

b. Estimation.

Potassa is weighed either as *sulphate of potassa*, as *chloride of potassium*, or as *bichloride of platinum and chloride of potassium* (see § 68). For the alkalimetric estimation of caustic or carbonated potassa, see §§ 207 and 208.

We may convert into

1. Sulphate of Potassa.

Salts of potassa with strong volatile acids; *e.g.*, chloride of potassium, bromide of potassium, nitrate of potassa, &c., and salts with organic acids.

2. Chloride of Potassium.

In general, caustic potassa and salts of potassa with weak volatile acids; also, and more particularly, sulphate, chromate, chlorate, and silicate of potassa.

3. Bichloride of Platinum and Chloride of Potassium.

Salts of potassa with non-volatile acids soluble in alcohol; *e.g.*, phosphate of potassa, borate of potassa.

The potassa in the borate of that alkali may be determined also as sulphate (§ 136); and the potassa in the phosphate, as chloride of potassium (§ 135).

The form of bichloride of platinum and chloride of potassium may also be resorted to in general, for the estimation of the potassa in all salts of that alkali with acids soluble in alcohol. This form is, moreover, of especial importance, as that in which the separation of potassa from soda, &c., is effected.

1. *Determination as Sulphate of Potassa.*

Evaporate the aqueous solution of the sulphate of potassa to dryness, ignite the residue in a platinum crucible or dish, and weigh (§ 42). The residue must be thoroughly dried before you proceed to ignite it; the heat applied for the latter purpose must be moderate at first, and very gradually increased to the requisite degree; the crucible or dish must be kept well covered—neglect of these precautionary rules involves always a loss of substance from decrepitation. If free sulphuric acid is present, we obtain, upon evaporation, bisulphate of potassa; in such cases the excess of sulphuric acid is to be removed by igniting first alone (here it is best to place the lamp so that the flame may strike the dish-cover obliquely from above), then with carbonate of ammonia. See § 68.

For properties of the residue, see § 68. Observe more particularly that the residue must dissolve to a clear fluid, and that the solution must be neutral. Should traces of platinum remain behind (the dish not having been previously weighed) these must be carefully determined, and their weight subtracted from that of the ignited residue.

With proper care and attention, this method gives accurate results.

To convert the above-mentioned salts (chloride of potassium, &c.) into sulphate of potassa, add to their aqueous solution a quantity of pure sulphuric acid more than sufficient to saturate the whole of the potassa, evaporate the solution to dryness, ignite the residue, and convert the bisulphate of potassa into the neutral salt, by treating with carbonate of ammonia (§ 68).

As the expulsion of a large quantity of sulphuric acid is a very disagreeable process, avoid adding too great an excess. Should too little of the acid have been used, which you may infer from the non-evolution of sulphuric acid fumes on ignition, moisten the residue with dilute sulphuric acid, evaporate, and again ignite. If you have to deal with a small quantity only of chloride of potassium, &c., proceed at once to treat the dry salt, cautiously, with dilute sulphuric acid in the platinum crucible; provided the latter be capacious enough. In the case of bromide and iodide of potassium, the use of platinum vessels must be avoided.

[Potassa salts with organic acids are directly converted into sulphate of potassa by first carbonizing them at the lowest possible temperature, and after cooling adding some crystals of pure sulphate of ammonia and a little water to the mass. The crucible being covered, the water is evaporated by heating the crucible cover, and the whole is afterwards heated to dull redness, until the excess of sulphate of ammonia is destroyed. If the carbon is not fully consumed by this operation, add a little nitrate of ammonia and repeat the ignition. Kämmerer.[*]]

2. *Determination as Chloride of Potassium.*

General method the same as described in 1. The residue of chloride

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[* Fres. Zeit. VII. 222.]

of potassium must, previously to ignition, be treated in the same way as sulphate of potassa, and for the same reason. The salt must be heated in a well-covered crucible or dish, and only to dull redness, as the application of a higher degree of heat is likely to cause some loss by volatilization. No particular regard need be had to the presence of free acid. For properties of the residue, see § 68. This method, if properly and carefully executed, gives very accurate results. The chloride of potassium may, instead of being weighed, be determined volumetrically by § 141, *b*. This method, however, has no advantage in the case of single estimations, but saves time when a series of estimations has to be made.

In determining potassa in the carbonate it is sometimes desirable to avoid the effervescence occasioned by treatment with hydrochloric acid, as, for instance, in the case of the ignited residue of a potassa salt with an organic acid, which is contained in the crucible. This may be effected by treating the carbonate with solution of chloride of ammonium in excess, evaporating and igniting, when carbonate of ammonia and the excess of chloride of ammonium will escape, leaving chloride of potassium behind.

The methods of converting into chloride of potassium the potassa compounds specified above, will be found in Part II. of this Section, under the respective heads of the acids which they contain.

3. *Determination as Bichloride of Platinum and Chloride of Potassium.*

α. Salts of potassa with volatile acids (nitric acid, acetic acid, &c.).

Mix the solution with hydrochloric acid, evaporate to dryness, dissolve the residue in a little water, add a concentrated solution of bichloride of platinum, as neutral as possible, in excess, and evaporate in a porcelain dish, on the water-bath, nearly to dryness, taking care not to heat the water-bath quite to boiling. Pour spirit of wine of about 80 per cent. over the residue; let it stand for some time, and then transfer the bichloride of platinum and chloride of potassium, which remains undissolved, to a weighed filter (which may be readily done by means of a washing bottle filled with spirit of wine). Wash with spirit of wine, dry at 100°, and weigh (§ 50).

β. Potassa salts with non-volatile acids (phosphoric acid, boracic acid, &c.).

Make a concentrated solution of the salt in water, add some hydrochloric acid, and bichloride of platinum in excess, mix with a tolerable quantity of the strongest alcohol, let the mixture stand 24 hours; after which filter, and proceed as directed in *α*.

Properties of the precipitate, § 68. This method, if properly executed, gives satisfactory results. Still there is generally a trifling loss of substance, bichloride of platinum and chloride of potassium not being absolutely insoluble even in strong alcohol. In accurate analyses, therefore, the alcoholic washings must be evaporated, with addition of a little pure chloride af sodium, at a temperature not exceeding 75°, nearly to dryness, and the residue treated once more with spirit of wine. A trifling additional amount of bichloride of platinum and chloride of potassium is thus obtained, which is either added to the principal precipitate or collected on a separate small filter, and determined as platinum, by the method given below. The object of the addition of a little chloride of sodium to the bichloride of platinum is to obviate the decomposition to which pure bichloride of platinum is more liable, upon evaporation in alcoholic solution, than the bichloride containing sodio-bichloride of platinum. The atmosphere of a laboratory often contains ammonia, which might give rise to the formation of some chloride of platinum and ammonium, and to a consequent increase of weight in the potassium salt.

As collecting a precipitate upon a weighed filter is a rather tedious process, and, besides, not over accurate, where we have to deal with minute quantities of substance, it is better to collect small portions (up to about 0·03 grm.) of bichloride of platinum and chloride of potassium upon a very small *unweighed* filter,—dry, and transfer the filter, with the precipitate wrapped up in it, to a small porcelain crucible. Cover the crucible, and let the filter slowly char; remove the cover, burn the carbon of the filter, and let the crucible get cold. Put now a very minute portion of pure oxalic acid into the crucible, cover, and ignite, gently at first, finally to a strong red heat. The addition of the oxalic acid greatly promotes the complete decomposition of the bichloride of platinum and chloride of potassium, which cannot well be effected by simple ignition. Treat the contents of the crucible now with water, and wash the residuary platinum, until the last rinsings remain clear upon addition of solution of nitrate of silver.* Dry the residuary platinum, ignite, and weigh. One equivalent of platinum represents one equivalent of potassium.

§ 98.

2. Soda.

a. Solution

See § 97, *a*—solution of potassa—all the directions given in that place applying equally to the solution of soda and its salts.

b. Determination.

Soda is determined either as *sulphate of soda*, as *chloride of sodium*, or as *carbonate of soda* (§ 69). For the alkalimetric estimation of caustic soda, and carbonate of soda, see §§ 207 and 208.

We may convert into

1. Sulphate of Soda; 2. Chloride of Sodium.

In general the salts of soda corresponding to the salts of potassa specified under the analogous potash compounds, § 97.

3. Carbonate of Soda.

Caustic soda, bicarbonate of soda, and salts of soda with organic acids, also nitrate of soda and chloride of sodium.

In the borate of soda the alkali is estimated best as sulphate of soda (§ 136); in the phosphate, as chloride of sodium, or carbonate of soda (§ 135).

Salts of soda with organic acids are determined either, like the corresponding potassa compounds, as chloride, or—by preference—as carbonate. (This latter method is not so well adapted for salts of potassa.)

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* The washing of the residuary platinum may generally be effected by simple decantation.

The analyst must here bear in mind, that when carbon acts on fusing carbonate of soda, carbonic oxide escapes, and caustic soda in not inconsiderable quantity is formed.

1. *Determination as Sulphate of Soda.*

If alone and in aqueous solution, evaporate to dryness, ignite and weigh the residue in a covered platinum crucible (§ 42). The process does not involve any risk of loss by decrepitation, as in the case of sulphate of potassa. If free sulphuric acid happens to be present, this is removed in the same way as in the case of sulphate of potassa.

With regard to the conversion of chloride of sodium, &c., into sulphate of soda, see § 97, *b*, 1. For properties of the residue, see § 69. The method is easy, and gives accurate results.

2. *Determination as Chloride of Sodium.*

Same method as described in 1. The rules given and the observations made in § 97, *b*, 2, apply equally here. For properties of the residue see § 69.

The methods of converting the sulphate, chromate, chlorate, and silicate of soda into chloride of sodium, will be found in Part II. of this Section, under the respective heads of the acids which these salts contain.

3. *Determination as Carbonate of Soda.*

Evaporate the aqueous solution, ignite moderately, and weigh. The results are perfectly accurate. For properties of the residue, see § 69.

Caustic soda is converted into the carbonate by adding to its aqueous solution carbonate of ammonia in excess, evaporating at a gentle heat, and igniting the residue.

Bicarbonate of soda, if in the dry state, is converted into the carbonate by ignition. The heat must be very gradually increased, and the crucible kept well covered. If in aqueous solution, it is evaporated to dryness, in a capacious silver or platinum dish, and the residue ignited.

Salts of soda with organic acids are converted into the carbonate by ignition in a covered platinum crucible, from which the lid is removed after a time. The heat must be increased very gradually. When the mass has ceased to swell, the crucible is placed obliquely, with the lid leaning against it (see § 52, fig. 42), and a dull red heat applied until the carbon is consumed as far as practicable. The contents of the crucible are then warmed with water, and the fluid is filtered off from the residuary carbon, which is carefully washed. The filtrate and rinsings are evaporated to dryness with the addition of a little carbonate of ammonia, and the residue is ignited and weighed. The carbonate of ammonia is added, to convert any caustic soda that may have been formed into carbonate. The method, if carefully conducted, gives accurate results; however, a small loss of soda on carbonization is not to be avoided.

Nitrate of soda, or chloride of sodium, may be converted into carbonate, by adding to their aqueous solution perfectly pure oxalic acid in moderate excess, and evaporating several times to dryness, with repeated renewal of the water. All the nitric acid of the nitrate of soda escapes in this process, (partly decomposed, partly undecomposed); and equally so all the hydrochloric acid in the case of chloride of sodium. If the residue is now ignited until the excess of oxalic acid is removed, carbonate of soda is left.

§ 99

3. AMMONIA.

a. Solution.

Ammonia is soluble in water, as are all its salts with those acids which claim our attention here. It is not always necessary, however, to dissolve the ammoniacal salts for the purpose of determining the amount of ammonia contained in them.

b. Determination.

Ammonia is weighed, as stated § 70, either in the form of *chloride of ammonium*, or in that of *bichloride of platinum and chloride of ammonium*. Into these forms it may be converted either *directly* or *indirectly* (*i.e.*, after expulsion as ammonia, and re-combination with an acid). Ammonia is also frequently determined by volumetric analysis, and its quantity is sometimes inferred, from the volume of nitrogen.

We convert directly into

1. CHLORIDE OF AMMONIUM.

Ammoniacal gas and its aqueous solution, and also ammoniacal salts with weak volatile acids (carbonate of ammonia, sulphide of ammonium, &c.).

2. BICHLORIDE OF PLATINUM AND CHLORIDE OF AMMONIUM.

Ammoniacal salts with acids soluble in alcohol, such as sulphate of ammonia, phosphate of ammonia, &c.

3. The methods based on the EXPULSION OF THE AMMONIA from its compounds, and also that of inferring the amount of ammonia from the volume of nitrogen eliminated in the dry way, are equally applicable to all ammoniacal salts.

The expulsion of ammonia in the dry way, (by ignition with soda-lime,) and the estimation of that alkali from the volume of nitrogen eliminated in the dry way, being effected in the same manner as the estimation of the nitrogen in organic compounds, I refer the student to the Section on organic analysis. Here I shall only give the methods based upon the expulsion of ammonia and of nitrogen in the wet way. For the alkalimetric estimation of free ammonia, see §§ 207 and 208.

1. *Determination as Chloride of Ammonium.*

Evaporate the aqueous solution of the chloride of ammonium on the water-bath, and dry the residue at 100° until the weight remains constant (§ 42). The results are accurate. The volatilization of the chloride is very trifling. A direct experiment gave 99·94 instead of 100. (See Expt. 15.) The presence of free hydrochloric acid makes no difference; the conversion of caustic ammonia into chloride of ammonium may accordingly be effected by supersaturating with hydrochloric acid. The same applies to the conversion of the carbonate, with this addition only, that the process of supersaturation must be conducted in an obliquely-placed flask, and the mixture heated in the same, till the carbonic acid is driven off. In the analysis of sulphide of ammonium we proceed in the same way, taking care simply, after the expulsion of the sulphuretted hydrogen, and before proceeding to evaporate, to filter off the sulphur which may have separated. Instead of weighing the chloride of ammonium, its quantity may be inferred by the determination of its chlorine according to § 141, *b*. (Comp. chloride of potassium, § 97, *b*, 3).

2. *Determination as Bichloride of Platinum and Chloride of Ammonium.*

α. Ammoniacal salts with volatile acids.

Same method as described in § 97, *b*, 4, *α* (bichloride of platinum and chloride of potassium).

β. Ammoniacal salts with non-volatile acids.

Same method as described § 97, *b*, 4, *β* (bichloride of platinum and chloride of potassium). The results obtained by these methods are accurate.

If you wish to control the results,* ignite the double chloride, wrapped up in the filter, in a covered crucible, and calculate the amount of ammonia from that of the residuary platinum. The results must agree. The heat must be increased very gradually.† Want of due caution in this respect is apt to lead to loss, from particles of the double salt being carried away with the chloride of ammonium. Very small quantities of bichloride of platinum and chloride of ammonium are collected on an unweighed filter, dried, and at once reduced to platinum by ignition.‡

3. *Estimation by Expulsion of the Ammonia in the Wet Way.*

This method, which is applicable in all cases, may be effected in two different ways—viz.,

a. Expulsion of the Ammonia by distillation with Solution of Potassa, or Soda, or with Milk of Lime.—Applicable in all cases where no nitrogenous organic matters from which ammonia might be evolved upon boiling with solution of potassa, etc., are present with the ammonia salts.

Weigh the substance under examination in a small glass tube, 3 centimetres long and one wide, and put the tube, with the substance in it, into a flask containing a suitable quantity of moderately concentrated solution of potassa or soda, or milk of lime, from which every trace of ammonia has been removed by protracted ebullition, but which has been allowed to get thoroughly cold again; place the flask in a slanting position on wire-gauze, and immediately connect it by means of a glass tube bent at an obtuse angle, with the glass tube of a small cooling apparatus. Connect the lower end of this tube, by means of a tight-fitting perforated cork, with a sufficiently large tubulated receiver which is in its turn connected with a U tube by means of a bent tube passing through its tubulure.

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* If the bichloride of platinum and chloride of ammonium is pure, which may be known by its color and general appearance, this control may be dispensed with.

† The best way is to continue the application of a moderate heat for a long time, then to remove the lid, place the crucible obliquely, with the lid leaning against it, and burn the charred filter at a gradually increased heat (H. Rose).

‡ In a series of experiments to get the platinum from pure and perfectly anhydrous ammonio-bichloride of platinum, by very cautious ignition, Mr. Lucius, one of my pupils, obtained from 44·1 to 44·3 per cent. of the metal, instead of 44·3.

If you wish to *determine volumetrically the quantity of ammonia expelled*, introduce the larger portion of a measured quantity of standard solution of sulphuric or of nitric acid (§ 204), into the receiver, the remainder into the U tube; add to the portion of fluid in the latter a little water, and color the liquids in the receiver and U tube red with 1 or 2 c. c. of tincture of litmus. The cooling tube must not dip into the fluid in the receiver; the fluid in the U tube must completely fill the lower part, but it must not rise high, as otherwise the passage of air bubbles might easily occasion loss by spirting. The quantity of acid used must of course be more than sufficient to fix the whole of the ammonia expelled.

When the apparatus is fully arranged, and you have ascertained that all the joints are perfectly tight, heat the contents of the flask to gentle ebullition, and continue the application of the same degree of heat until the drops, as they fall into the receiver, have for some time altogether ceased to impart the least tint of blue to the portión of the fluid with which they first come in contact. Loosen the cork of the flask, allow to stand half an hour, pour the contents of the receiver and U tube into a beaker, rinsing out with small quantities of water, determine finally with a standard solution of soda the quantity of acid still free, which, by simple subtraction, will give the amount of acid which has combined with the ammonia; and from this you may now calculate the amount of the latter (§ 204). Results accurate.*

If you wish to *determine by the gravimetric method the quantity of ammonia expelled*, receive the ammonia evolved in a quantity of hydrochloric acid more than sufficient to fix the whole of it, and determine the chloride of ammonium formed, either by simple evaporation, after the directions of 1, or as ammonio-bichloride of platinum, after the directions of 2.

b. EXPULSION OF THE AMMONIA BY MILK OF LIME, WITHOUT APPLICATION OF HEAT.—This method, recommended by SCHLÖSING, is based upon the fact that an aqueous solution containing free ammonia gives off the latter completely, and in a comparatively short time, when exposed in a shallow vessel to the air, at the common temperature. It finds application in cases where the presence of organic nitrogenous substances, decomposable by boiling alkalies, forbids the use of the method described in 3, *a*; thus, for instance, in the estimation of the ammonia in urine, manures, &c.

The fluid containing the ammonia, the volume of which must not exceed 35 c. c., is introduced into a shallow flat-bottomed vessel from 10 to 12 centimetres in diameter; this vessel is put on a plate filled with mercury. A tripod, made of a massive glass rod, is placed in the vessel which contains the solution of the ammoniacal salt, and a saucer or shallow dish with 10 c. c. of the normal solution of oxalic or sulphuric acid (§ 204) put on it. A beaker is now inverted over the whole. The beaker is lifted up on one side as far as is required, and a sufficient quantity of milk of lime added by means of a pipette (which should not be drawn out at the lower end). The beaker is then rapidly pressed down, and weighted with a stone slab. After forty-eight hours the glass is lifted up, and a slip of moist reddened litmus paper placed in it; if no change of color is observable, this is a sign that the expulsion of the ammonia is complete; in the contrary case, the glass must be replaced. Instead of the beaker and plate with mercury, a bell-jar, with a ground and greased rim, placed air-tight on a level glass plate, may be used. A bell-jar, having at the top a tubular opening, furnished with a close-fitting glass stopper, answers the purpose best, as it permits the introduction of a slip of red litmus paper suspended from a thread; thus enabling the operator to see whether the combination of the ammonia with the acid is completed, without the necessity of removing the bell-jar. According to SCHLÖSING, forty-eight hours are always sufficient to expel 0·1 to 1 gramme of ammonia from 25 to 35 c. c. of solution. However, I can admit this statement only as regards quantities up to 0·3 grm.; quantities above this often require a longer time. I, therefore, always prefer operating with quantities of substance containing no more than 0·3 grm. ammonia at the most.

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* [In thus estimating minute quantities of ammonia, the condensing tube must be of tin, since glass yields a sensible amount of alkali to hot water vapor.]

When all the ammonia has been expelled, and has entered into combination with the acid, the quantity of acid left free is determined by means of standard solution of soda, and the amount of the ammonia calculated from the result (§ 204).

4. *Estimation by Expulsion of the Nitrogen in the Wet Way.*

A process for determining ammonia by means of the azotometer has been given by W. KNOP.* It depends on the separation of the nitrogen by a bromized and strongly alkaline solution of hypochlorite of soda.†

[The simplest azotometer is that described by RUMPF.‡ It consists of a burette of 50 or 100 c. c. stationed in a glass cylinder nearly filled with mercury, and connected by a stout caoutchouc tube with a small bottle, *a*, fig. 46, to which is fitted a soft thrice-perforated caoutchouc stopper. The stopper carries a thermometer and two short glass tubes, one of which joins it to the burette, and the other has attached a short bit of caoutchouc tubing and a pinch-cock, *e*. The weighed ammonia salt (not more than 0·4 grm.) is placed in the tube, *f*, with 10 c. c. of water, and 50· c. c. of the bromized hypochlorite solution are brought into the bottle, *a*. The cock, *e*, being open, the stopper is firmly fixed in its place, and the burette is depressed in the mercury until its uppermost degree exactly coincides with the surface of the metal. The cock is then closed,

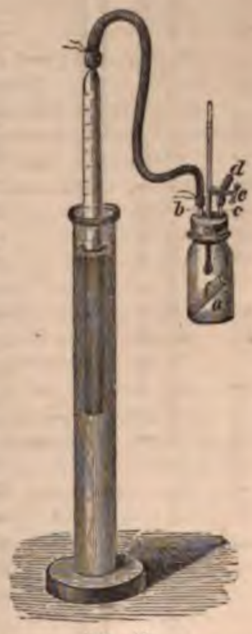

Fig. 46.

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[*] Chem. Centralbl. 1860, 244.

[†] This is prepared as follows:—Dissolve 1 part of carbonate of soda in 15 parts of water, cool the fluid with ice, saturate perfectly with chlorine, keeping cold all the while, and add strong soda solution (of 25 per cent.) till the mixture on rubbing between the fingers makes the skin slippery. Before using, add to the quantity required for the series of experiments bromine in the proportion of 2–3 grm. to the litre, and shake.

[‡] Fres. Zeit., VI. 398.

Evolved..........	1	2	3	4	5	6	7	8	9	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Absorbed.........	0.06	0.08	0.11	0.13	0.16	0.18	0.21	0.23	0.26	0.28	0.31	0.33	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Evolved..........	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
Absorbed.........	0.56	0.58	0.61	0.63	0.66	0.68	0.71	0.73	0.76	0.78	0.81	0.83	0.86	0.88	0.91	0.93	0.96	0.98	1.01	1.03
Evolved..........	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Absorbed.........	1.06	1.08	1.11	1.13	1.16	1.18	1.21	1.23	1.26	1.28	1.31	1.33	1.36	1.38	1.41	1.43	1.46	1.48	1.51	1.53
Evolved..........	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80
Absorbed.........	1.56	1.58	1.61	1.63	1.66	1.68	1.71	1.73	1.76	1.78	1.81	1.83	1.86	1.88	1.91	1.93	1.96	1.98	2.01	2.03
Evolved..........	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
Absorbed.........	2.06	2.08	2.11	2.13	2.16	2.18	2.21	2.23	2.26	2.28	2.31	2.33	2.36	2.38	2.41	2.43	2.46	2.48	2.51	2.53

and the bottle is inclined to bring the two substances in contact. The ammonia salt is speedily decomposed. When no further evolution of gas takes place the burette is so adjusted that the level of the mercury without and within it shall nearly coincide, and the operator waits 10–20 minutes, or until the thermometer in *a* indicates the same temperature as the surrounding air. Then the adjustment of the burette to exact coincidence of the mercury level, within and without, is effected, and the volume of the gas is read off. The stand of the thermometer and barometer are also noted, and the recorded volume of nitrogen is corrected by use of the tables on pp. 160 and 162–163, by DIETRICH:

The first table gives a correction for the nitrogen which is absorbed by the 60 c. c. of liquid in the bottle *a*. The amount varies with the relative volumes of air and nitrogen, and is determined empirically by decomposing known quantities of ammonia and noting the difference between the obtained and the theoretical volume of nitrogen. The correction holds strictly, of course, only for a solution of such strength as that employed by DIETRICH and at the mean temperatures.

The second table serves to spare the labor of calculation. The weight of 1 c. c. of nitrogen, measured e. g. at 754 mm. of barometer and 15° C., is found at the intersection of the vertical column 754 with the horizontal column 15°, is, viz., 1·16187.

To the observed volume of nitrogen add the amount absorbed as per Table I., and correct the total by Table II. It scarcely requires to be mentioned that good results can only be obtained in an apartment where the temperature is uniform, and when care is exercised to avoid warming the apparatus in handling. See DIETRICH's papers.*

§ 100.

Supplement to the First Group.

LITHIA.

In the absence of other bases, lithia may, like potassa and soda, be converted into anhydrous SULPHATE, and weighed in that form ($Li\,O, S\,O_3$). As lithia forms no acid sulphate, the excess of sulphuric acid may be readily removed by simple ignition. CARBONATE OF LITHIA also, which is difficultly soluble in water, and fuses at a red heat without suffering decomposition, is well suited for weighing; whilst chloride of lithium, which deliquesces in the air, and is by ignition in moist air converted into hydrochloric acid and lithia, is unfit for the estimation of lithia.

In presence of other alkalies, lithia is best converted into BASIC PHOSPHATE OF LITHIA ($3\,Li\,O, P\,O_5$), and weighed in that form. This is effected by the following process: add to the solution a sufficient quantity of phosphate of soda (which must be perfectly free from phosphates of the alkaline earths), and enough soda to keep the reaction alkaline, and evaporate the mixture to dryness; pour water over the residue, in sufficient quantity to dissolve the soluble salts with the aid of a gentle

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* Fres. Zeit. III. 162.; IV. 141, and V. 36.

II. TABLE OF THE WEIGHT OF A

In Milligrammes for Pressures from 720 *to* 770 *mm.*

MILLIMETRES.

TEMPERATURE CELSIUS.	720	722	724	726	728	730	732	734	736	738	740	742	744
10°	1.13380	1.13699	1.14018	1.14337	1.14656	1.14975	1.15294	1.15613	1.15932	1.16251	1.16570	1.16889	1.17208
11°	1.12881	1.13199	1.13517	1.13835	1.14153	1.14471	1.14789	1.15107	1.15424	1.15742	1.16060	1.16378	1.16696
12°	1.12376	1.12693	1.13010	1.13326	1.13643	1.13960	1.14277	1.14593	1.14910	1.15227	1.15543	1.15860	1.16177
13°	1.11875	1.12191	1.12506	1.12822	1.13138	1.13454	1.13769	1.14085	1.14401	1.14716	1.15032	1.15348	1.15663
14°	1.11369	1.11684	1.11999	1.12313	1.12628	1.12942	1.13257	1.13572	1.13886	1.14201	1.14515	1.14830	1.15145
15°	1.10859	1.11172	1.11486	1.11799	1.12113	1.12426	1.12739	1.13053	1.13366	1.13680	1.13993	1.14306	1.14620
16°	1.10346	1.10658	1.10971	1.11283	1.11596	1.11908	1.12220	1.12533	1.12845	1.13158	1.13470	1.13782	1.14095
17°	1.09828	1.10139	1.10450	1.10761	1.11073	1.11384	1.11695	1.12006	1.12317	1.12629	1.12940	1.13251	1.13562
18°	1.09304	1.09614	1.09924	1.10234	1.10544	1.10854	1.11165	1.11475	1.11785	1.12095	1.12405	1.12715	1.13025
19°	1.08744	1.09083	1.09392	1.09702	1.10011	1.10320	1.10629	1.10938	1.11248	1.11557	1.11866	1.12175	1.12484
20°	1.08246	1.08554	1.08862	1.09170	1.09478	1.09786	1.10094	1.10402	1.10710	1.11018	1.11327	1.11635	1.11943
21°	1.07708	1.08015	1.08322	1.08629	1.08936	1.09243	1.09550	1.09857	1.10165	1.10472	1.10779	1.11086	1.11393
22°	1.07166	1.07472	1.07778	1.08084	1.08390	1.08696	1.09002	1.09308	1.09614	1.09921	1.10227	1.10533	1.10839
23°	1.06616	1.06921	1.07226	1.07531	1.07836	1.08141	1.08446	1.08751	1.09056	1.09361	1.09666	1.09971	1.10276
24°	1.06061	1.06365	1.06669	1.06973	1.07277	1.07581	1.07885	1.08189	1.08493	1.08796	1.09100	1.09404	1.09708
25°	1.05499	1.05801	1.06104	1.06407	1.06710	1.07013	1.07316	1.07619	1.07922	1.08225	1.08528	1.08831	1.09134
	720	722	724	726	728	730	732	734	736	738	740	742	744

MILLIMETRES.

CUBIC CENTIMETRE OF NITROGEN.

of Mercury, and for Temperatures from 10° *to* 25° *C.*

MILLIMETRES.

746	748	750	752	754	756	758	760	762	764	766	768	770	TEMPERATURE CELSIUS.
1.17527	1.17846	1.18165	1.18484	1.18803	1.19122	1.19441	1.19760	1.20079	1.20398	1.20717	1.21036	1.21355	10°
1.17014	1.17332	1.17650	1.17168	1.18286	1.18603	1.18921	1.19239	1.19557	1.19875	1.20193	1.20511	1.20829	11°
1.16493	1.16810	1.17127	1.17444	1.17760	1.18077	1.18394	1.18710	1.19027	1.19344	1.19660	1.19977	1.20294	12°
1.15979	1.16295	1.16611	1.16926	1.17242	1.17558	1.17873	1.18189	1.18505	1.18820	1.19136	1.19452	1.19768	13°
1.15459	1.15774	1.16088	1.16403	1.16718	1.17032	1.17347	1.17661	1.17976	1.18291	1.18605	1.18920	1.19234	14°
1.14933	1.15247	1.15560	1.15873	1.16187	1.16500	1.16814	1.17127	1.17440	1.17754	1.18067	1.18381	1.18694	15°
1.14407	1.14720	1.15032	1.15344	1.15657	1.15969	1.16282	1.16594	1.16906	1.17219	1.17531	1.17844	1.18156	16°
1.12873	1.14185	1.14496	1.14807	1.15118	1.15429	1.15741	1.16052	1.16363	1.16674	1.16985	1.17297	1.17608	17°
1.13335	1.13645	1.13955	1.14266	1.14576	1.14886	1.15196	1.15506	1.15816	1.16126	1.16436	1.16746	1.17056	18°
1.12794	1.13103	1.13412	1.13721	1.14030	1.14340	1.14649	1.14958	1.15267	1.15576	1.15886	1.16195	1.16504	19°
1.12251	1.12559	1.12867	1.13175	1.13483	1.13791	1.14099	1.14408	1.14716	1.15024	1.15332	1.15640	1.15948	20°
1.11700	1.12007	1.12314	1.12621	1.12928	1.13236	1.13543	1.13850	1.14157	1.14464	1.14771	1.15078	1.15385	21°
1.11145	1.11451	1.11757	1.12063	1.12369	1.12675	1.12982	1.13288	1.13594	1.13900	1.14206	1.14512	1.14818	22°
1.10581	1.10886	1.11191	1.11496	1.11801	1.12106	1.12411	1.12716	1.13021	1.13326	1.13631	1.13936	1.14241	23°
1.10012	1.10316	1.10620	1.10924	1.11228	1.11532	1.11835	1.12139	1.12443	1.12747	1.13051	1.13355	1.13659	24°
1.09437	1.09740	1.10043	1.10346	1.10649	1.10952	1.11255	1.11558	1.11861	1.12164	1.12467	1.12770	1.13073	25°
746	748	750	752	754	756	758	760	762	764	766	768	770	

MILLIMETRES.

heat, add an equal volume of solution of ammonia, digest at a gentle heat, filter after twelve hours, and wash the precipitate with a mixture of equal volumes of water and solution of ammonia. Evaporate the filtrate and first washings to dryness, and treat the residue in the same way as before. If some more phosphate of lithia is thereby obtained, add this to the principal quantity. The process gives, on an average, 99·61 for 100 parts of lithia.

If the quantity of lithia present is relatively very small, the larger portion of the potassa or soda compounds should first be removed by addition of absolute alcohol to the most highly concentrated solution of the salts (chlorides, bromides, iodides, or nitrates, but not sulphates); since this, by lessening the amount of water required to effect the separation of the phosphate of lithia from the soluble salts, will prevent loss of lithia (W. MAYER*).

The precipitated basic phosphate of lithia has the formula $3\,Li\,O, P\,O_5 + aq.$ It dissolves in 2539 parts of pure, and 3920 parts of ammoniated water; at 100°, it completely loses its water; if pure, it does not cake at a moderate red heat (MAYER).

The objections raised by RAMMELSBERG† to MAYER's method of estimating lithia I find to be ungrounded. According to my own experience, it appears that the filtrate and wash-water must be evaporated in a platinum dish not only once, but at least twice—in fact, till a residue is obtained which is completely soluble in dilute ammonia. Phosphate of lithia may be dried at 100°, or ignited according to § 53, before being weighed. In the latter case, care must be taken to free the filter as much as possible from the precipitate before proceeding to incinerate it. I have thus obtained,‡ instead of 100 parts carbonate of lithia, by drying at 100°, 99·84, 99·89, 100·41,—by igniting 99·66 and 100·05. The phosphate of lithia obtained was free from soda.

SECOND GROUP.

BARYTA—STRONTIA—LIME—MAGNESIA.

§ 101.

1. BARYTA.

a. Solution.

Caustic baryta is soluble in water, as are many of the salts of this alkaline earth. The salts of baryta which are insoluble in water are, with almost the single exception of the sulphate, readily dissolved by dilute hydrochloric acid. The solution of the sulphate is effected by fusion with carbonate of soda, &c. (See § 132.)

b. Determination.

Baryta is weighed either as *sulphate* or as *carbonate*, rarely (in the separation from strontia) as *silico-fluoride of barium* (§ 71). Baryta in the pure state, or in form of carbonate, may also be determined by the volumetric (alkalimetric) method. Comp. § 210.

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* Annal. der Chem. u. Pharm. 98, 193, where Mayer has also demonstrated the non-existence of a phosphate of soda and lithia of fixed composition (Berzelius), or of varying composition (Rammelsberg).

† Pogg. Annal. 102, 443.

‡ Zeitschr. f. Analyt. Chem. 1, 42.

We may convert into

1. Sulphate of Baryta.

a. By Precipitation.	*b. By Evaporation.*
All compounds of baryta without exception.	All compounds of baryta with volatile acids, if no other non-volatile body is present.

2. Carbonate of Baryta.

a. All salts of baryta soluble in water.

b. Salts of baryta with organic acids.

Baryta is both precipitated and weighed, by far the most frequently as sulphate, the more so as this is the form in which it is most conveniently separated from other bases. The determination by means of evaporation (1, *b*) is, in cases where it can be applied, and where we are not obliged to evaporate large quantities of fluid, very exact and convenient. Baryta is determined as carbonate in the wet way, when from any reason it is not possible or not desirable to precipitate it as sulphate. If a fluid or dry substance contains bodies which impede the precipitation of the baryta as sulphate or carbonate (alkaline citrates, metaphosphoric acid, see § 71, *a* and *b*), such bodies must of course be got rid of, before proceeding to precipitation.

1. *Determination as Sulphate of Baryta.*

a. By Precipitation.

Heat the moderately dilute solution of baryta, which must not contain too much free acid (and must, therefore, if necessary, first be freed therefrom by evaporation or addition of carbonate of soda), in a platinum or porcelain dish, or in a glass vessel, to incipient ebullition, add dilute sulphuric acid, as long as a precipitate forms, keep the mixture for some time at a temperature very near the boiling point, and allow the precipitate a few minutes to subside; decant the almost clear supernatant fluid on a filter, boil the precipitate three or four times with water, then transfer it to the filter, and wash with boiling water, until the filtrate is no longer rendered turbid by chloride of barium. Dry the precipitate, and treat it as directed in § 53. If the precipitate has been properly washed in the manner here directed, it is perfectly pure, and gives up no chloride of barium to acetic acid, even if boiling, nor any appreciable trace of it to boiling nitric acid, though the solution had contained that salt.*

b. By Evaporation.

Add to the solution, in a weighed platinum dish, pure sulphuric acid very slightly in excess, and evaporate on the water-bath; expel the excess of sulphuric acid by cautious application of heat, and ignite the residue.

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* I mention this in reference to Siegle's statement in the Journal f. prakt. Chem. 69, 142, that acetic acid and nitric acid will still extract small quantities of chloride of barium from sulphate of baryta, formed in presence of an excess of sulphuric acid, and thoroughly washed with water.

For the properties of sulphate of baryta, see § 71.

Both methods, if properly and carefully executed, give almost absolutely accurate results.

2. *Determination as Carbonate of Baryta.*

a. In Solutions.

Mix the moderately dilute solution of the baryta salt in a beaker with ammonia, add carbonate of ammonia in slight excess, and let the mixture stand several hours in a warm place. Filter, wash the precipitate with water mixed with a little ammonia, dry, and ignite (§ 53).

For the properties of the precipitate, see § 71. This method involves a trifling loss of substance, as the carbonate of baryta is not absolutely insoluble in water. The direct experiment, No. 62, gave 99·79 instead of 100.

If the solution contains a notable quantity of ammoniacal salts, the loss incurred is much more considerable, since the presence of such salts greatly increases the solubility of the carbonate of baryta.

b. In Salts of Baryta with Organic Acids.

Heat the salt slowly in a covered platinum crucible, until no more fumes are evolved; place the crucible obliquely, with the lid leaning against it, and ignite, until the whole of the carbon is consumed, and the residue presents a perfectly white appearance: moisten the residue with a concentrated solution of carbonate of ammonia, evaporate, ignite gently, and weigh. The results obtained by this method are quite satisfactory. A direct experiment, No. 63, gave 99·61 instead of 100. The loss of substance which almost invariably attends this method is owing to particles of the salt being carried away with the fumes evolved upon ignition, and is accordingly the less considerable, the more slowly and gradually the heat is increased. Omission of the moistening of the residue with carbonate of ammonia would involve a further loss of substance, as the ignition of carbonate of baryta in contact with carbon is attended with formation of some caustic baryta, carbonic oxide gas being evolved.

§ 102.

2. STRONTIA.

a. Solution.

See the preceding paragraph (§ 101, *a.*—Solution of baryta), the directions there given applying equally here.

b. Determination.

Strontia is weighed either as *sulphate* or as *carbonate of strontia* (§ 72). Strontia in the pure state, or in form of carbonate, may be determined also by the volumetric (alkalimetric) method. Comp. § 210.

We may convert into

1. Sulphate of Strontia.

a. By Precipitation.

All compounds of strontia without exception.

b. By Evaporation.

All salts of strontia with volatile acids, if no other non-volatile body is present.

2. Carbonate of Strontia.

α. All compounds of strontia soluble in water.

β. Salts of strontia with organic acids.

The method based on the precipitation of strontia with sulphuric acid yields accurate results only in cases where the fluid from which the strontia is to be precipitated may be mixed, without injury, with alcohol. Where this cannot be done, and where the method based on the evaporation of the solution of strontia with sulphuric acid is equally inapplicable, the conversion into the carbonate ought to be resorted to in preference, if admissible. As in the case of baryta, so here, we have to be on our guard against the presence of substances which would impede precipitation.

1. *Determination as Sulphate of Strontia.*

a. By Precipitation.

Mix the solution of the salt of strontia (which must not be too dilute, nor contain much free hydrochloric or nitric acid) with dilute sulphuric acid in excess, in a beaker, and add at least an equal volume of alcohol; let the mixture stand twelve hours, and filter; wash the precipitate with dilute spirit of wine, dry and ignite (§ 53).

If the circumstances of the case prevent the use of alcohol, the fluid must be precipitated in a tolerably concentrated state, allowed to stand in the cold* for at least twenty-four hours, filtered, and the precipitate washed with cold water, until the last rinsings manifest no longer an acid reaction, and leave no perceptible residue upon evaporation. If traces of free sulphuric acid remain adhering to the filter, the latter turns black on drying, and crumbles to pieces; too protracted washing of the precipitate, on the other hand, tends to increase the loss of substance.

Care must be taken that the precipitate be thoroughly dry, before proceeding to ignite it; otherwise it will be apt to throw off fine particles during the latter process. The filter, which is to be burnt apart from the precipitate, must be as clean as possible, or some loss of substance will be incurred; as may be clearly seen from the depth of the carmine tint of the flame with which the filter burns if the precipitate has not been properly removed.

For the properties of the precipitate, see § 72. When alcohol is used and the directions given are properly adhered to, the results are very accurate; when the sulphate of strontia is precipitated from an aqueous solution, on the contrary, a certain amount of loss is unavoidable, as sulphate of strontia is not absolutely insoluble in water. The direct experiments, No. 64, gave only 98·12 and 98·02 instead of 100. However, the error may be rectified, by calculating the amount of sulphate of strontia dissolved in the filtrate and the wash-water, basing the calculation upon the known degree of solubility of sulphate of strontia in pure and acidified water. See Expt. No. 65, which, with this correction, gave 99·77 instead of 100.

b. By Evaporation.

The same method as described for baryta, § 101, 1, *b*.

2. *Determination as Carbonate of Strontia.*

a. In Solutions.

The same method as described § 101, 2, *a*. For the properties of the precipitate, see § 72. The method gives very accurate results, as carbonate of strontia is nearly absolutely insoluble in water containing ammonia and carbonate of ammonia. A direct experiment, No. 66, gave 99·82 instead of 100. Presence of ammoniacal salts exercises here a less adverse influence than the precipitation of carbonate of baryta.

b. In Salts with Organic Acids.

The same method as described § 101, 2, *b*. The remarks made there, respecting the accuracy of the results, apply equally here.

§ 103.

3. LIME.

a. Solution.

See § 101, *a*.—Solution of baryta. Fluoride of calcium is, by means of sulphuric acid, converted into sulphate of lime, and the latter again, if necessary, decomposed by boiling or fusing with an alkaline carbonate (§ 132). [Sulphate of lime dissolves readily in moderately dilute hydrochloric acid. It is much less soluble in strong hydrochloric acid.]

b. Determination.

Lime is weighed either as *sulphate*, or as *carbonate of lime* (§ 73). It may be brought into the first form by evaporation, or by precipitation; into the latter, by precipitation as oxalate, or at once as carbonate, or by ignition.

Small quantities of lime are also occasionally reduced to the caustic state, instead of being converted into carbonate. Lime in the pure state, or in form of carbonate, may be determined also by the volumetric (alkalimetric) method. Comp. § 210.

We may convert into

1. SULPHATE OF LIME.

a. By Precipitation.

All salts of lime with acids soluble in alcohol, provided no other substance insoluble in alcohol be present.

b. By Evaporation.

All salts of lime with volatile acids, provided no non-volatile body be present.

2. Carbonate of Lime.

a. By Precipitation with Carbonate of Ammonia.

All salts of lime soluble in water.

b. By Precipitation with Oxalate of Ammonia.

All salts of lime soluble in water or in hydrochloric acid without exception.

c. By Ignition.

Salts of lime with organic acids.

Of these several methods, 2, *b* (precipitation with oxalate of ammonia) is the one most frequently resorted to. This, and the method 1, *b*, give the most accurate results. The method, 1, *a*, is usually resorted to only to effect the separation of lime from other bases; 2, *a*, generally only to effect the separation of lime together with other alkaline earths from the alkalies. As many bodies (alkaline citrates, and metaphosphates) interfere with the precipitation of lime by the precipitants given, these, if present, must be first removed.

1. *Determination as Sulphate of Lime.*

a. By Precipitation.

Mix the solution of lime in a beaker, with dilute sulphuric acid in excess, and add twice the volume of alcohol; let the mixture stand twelve hours, filter, and *thoroughly* wash the precipitate with spirit of wine, dry, and ignite moderately (§ 53). For the properties of the precipitate, see § 73. The results are very accurate. A direct experiment, No. 67, gave 99·64 instead of 100.

b. By Evaporation.

The same method as described § 101, **1**, *b*.

2. *Determination as Carbonate of Lime.*

a. By Precipitation with Carbonate of Ammonia.

The same method as described § 101, 2, *a*. The precipitate must be exposed only to a very gentle red heat, but this must be continued for some time. For the properties of the precipitate, see § 73.

This method gives very accurate results, the loss of substance incurred being hardly worth mentioning.

If the solution contains chloride of ammonium or similar ammoniacal salts in considerable proportion, the loss of substance incurred is far greater. The same is the case if the precipitate is washed with pure instead of ammoniacal water. A direct experiment, No. 68, in which pure water was used, gave 99·17 instead of 100 parts of lime.

b. By Precipitation with Oxalate of Ammonia.

α. The Lime Salt is soluble in Water.

To the hot solution in a beaker, add oxalate of ammonia in moderate excess, and then ammonia sufficient to impart an ammoniacal smell to the fluid; cover the glass, and let it stand in a warm place until the precipitate has completely subsided, which will require twelve hours, at least. Pour the clear fluid gently and cautiously, so as to leave the precipitate undisturbed, on a filter; wash the precipitate two or three times by decantation with hot water; lastly, transfer the precipitate also to the filter, by rinsing with hot water, taking care, before the addition of a fresh portion, to wait until the fluid has completely passed through the filter. Small particles of the precipitate, adhering firmly to the glass, are removed with a feather. If this fails to effect their complete removal, they should be dissolved in a few drops of highly dilute hydrochloric acid, ammonia added to the solution, and the oxalate obtained added to the first precipitate. Deviations from the rules laid down here will generally give rise to the passing of a turbid fluid through the filter. After having washed the precipitate, dry it on the filter in the funnel, and transfer the dry precipitate to a platinum crucible, taking care to remove it as completely as possible from the filter; burn the filter on a piece of platinum wire, letting the ash drop into the hollow of the lid; put the latter, now inverted, on the crucible, so that the filter ash may not mix with the precipitate; heat at first very gently, then more strongly, until the bottom of the crucible is heated to very faint redness. Keep it at that temperature from ten to fifteen minutes, removing the lid from time to time. I am accustomed during this operation to move the lamp backwards and forwards under the crucible with the hand, since, if you allow it to stand, the heat may very easily get too high. Finally allow to cool in the desiccator and weigh. After weighing, moisten the contents of the crucible, which must be perfectly white, or barely show the least tinge of gray, with a little water, and test this after a time with a minute slip of turmeric paper. Should the paper turn brown—a sign that the heat applied was too strong—rinse off the fluid adhering to the paper with a little water into the crucible, throw in a small lump of pure carbonate of ammonia, evaporate to dryness (best in the water-bath), heat to very faint redness, and weigh the residue. If the weight has increased, repeat the same operation until the weight remains constant. This method gives nearly absolutely accurate results; and if the application of heat is properly managed, there is no need of the tedious evaporation with carbonate of ammonia. A direct experiment, No. 69, gave 99·99 instead of 100.

For the properties of the precipitate and residue, see § 73.

If the quantity of oxalate of lime obtained is only very trifling, I prefer to convert it into caustic lime or into the sulphate. To effect the former, the oxalate of lime is heated to intense redness, in a small platinum crucible, over a gas blow-pipe flame for some time. The conversion of the oxalate into sulphate is effected most conveniently by SCHRÖTTER's method, viz., ignition with pure sulphate of ammonia.

Many chemists prefer collecting the oxalate of lime upon a weighed filter, and drying at 100°. Thus obtained it consists of $2\ CaO, C_4O_6 + 2\ aq$. This method, besides being more tedious, gives less accurate results

accurate
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of oxalic acid in

l. If the acid combined
is operation (*e.g.*, carbonic
poration (*e.g.*, silicic acid),
irected in *a*. But if the acid
phosphoric acid), proceed as fol-
begins to form, re-dissolve this
oxalate of ammonia in excess, and
recipitate to subside, and proceed for
directed in *a*. In this process the free
bines with the ammonia and soda of the
a corresponding quantity of oxalic acid and
oxalate of lime is nearly insoluble. The
results. A direct experiment, No. 72, gave

a.

as described § 101, 2, *b* (baryta). The residue re-
ration with carbonate of ammonia (which operation
perform twice) must be ignited very gently. The
§ 101, 2, *b*, in reference to the accuracy of the results,
ere. By way of control, the carbonate of lime may be
the caustic state or into sulphate of lime (see *b*, *a*), or it
rmined alkalimetrically (§ 210).

which are insoluble in that menstruum dissolve in hydrochloric acid, with the exception of some silicates and aluminates.

b. Determination.

Magnesia is weighed (§ 74) either as *sulphate* or as *pyrophosphate*, or as *pure magnesia*. In the pure state, or in form of carbonate, it may be determined also by the alkalimetric method described in § 210.

We may convert into

1. SULPHATE OF MAGNESIA.

a. Directly.	*b. Indirectly.*
All compounds of magnesia with volatile acids, provided no other non-volatile substance be present.	All compounds of magnesia soluble in water, and also those which, insoluble in that menstruum, dissolve in hydrochloric acid, with separation of their acid (provided no ammoniacal salts be present).

2. PYROPHOSPHATE OF MAGNESIA.

All compounds of magnesia without exception.

3. PURE MAGNESIA.

a. Salts of magnesia with organic acids, or with readily volatile inorganic oxygen acids.

b. Chloride of magnesium, and the compounds of magnesia convertible into that salt.

The direct determination as sulphate of magnesia is highly recommended in all cases where it is applicable. The indirect conversion into the sulphate serves only in the case of certain separations, and is hardly ever had recourse to where it can possibly be avoided. The determination as pyrophosphate is most generally resorted to; especially also in the separation of magnesia from other bases. The method based on the conversion of chloride of magnesium into pure magnesia is usually resorted to only to effect the separation of magnesia from the fixed alkalies. Compounds of magnesia with phosphoric acid are analyzed as § 134 directs.

1. *Determination as Sulphate of Magnesia.*

Add to the solution excess of pure dilute sulphuric acid, evaporate to dryness, in a weighed platinum dish, on the water-bath; then heat at first cautiously, afterwards, with the cover on more strongly—here it is advisable to place the lamp so that the flame may play obliquely on the cover from above—until the excess of sulphuric acid is completely expelled; lastly, ignite gently over the lamp for some time; allow to cool, and weigh. Should no fumes of hydrated sulphuric acid escape upon the application of a strongish heat, this may be looked upon as a sure sign that the sulphuric acid has not been added in sufficient quantity, in which case, after allowing to cool, a fresh portion of sulphuric acid is added. The method yields very accurate results. Care must be taken not to use a very large excess of sulphuric acid. The residue must be exposed to a moderate red heat only, and weighed rapidly. For the properties of the residue, see § 74.

2. *Determination as Pyrophosphate of Magnesia.*

The solution of the salt of magnesia is mixed, in a beaker, with chloride of ammonium, and ammonia added in slight excess. Should a precipitate form upon the addition of ammonia, this may be considered a sign that a sufficient amount of chloride of ammonium has not been used; a fresh amount of that salt must consequently be added, sufficient to effect the re-solution of the precipitate formed. The clear fluid is then mixed with a solution of phosphate of soda in excess, and the mixture stirred, taking care to avoid touching the sides of the beaker with the stirring-rod; otherwise particles of the precipitate are apt to adhere so firmly to the rubbed parts of the beaker, that it will be found difficult to remove them; the beaker is then covered, and allowed to stand at rest for twelve hours, without warming; after that time the fluid is filtered, and the precipitate collected on the filter, the last particles of it being rinsed out of the glass with a portion of the filtrate, with the aid of a feather; when the fluid has completely passed through, the precipitate is washed with a mixture of 3 parts of water, and 1 part of solution of ammonia of 0·96 sp. gr., the operation being continued until a few drops of the fluid passing through the filter mixed with nitric acid and a drop of nitrate of silver show only a very slight opalescence.

The precipitate is now thoroughly dried, and then transferred to a platinum crucible (§ 53); the latter, with the lid on, is exposed for some time to a very gentle heat, which is finally increased to intense redness. The filter, as clean as practicable, is incinerated in a spiral of platinum wire, and the ash transferred to the crucible, which is then once more exposed to a red heat, allowed to cool, and weighed.

For the properties of the precipitate and residue, see § 74.

This method, if properly executed, yields most accurate results. The precipitate must be washed completely, but not over-washed, and the washing water must always contain the requisite quantity of ammonia.

Direct experiments, No. 73, *a* and *b*, gave respectively 100·43 and 100·30 instead of 100.

3. *Determination as pure Magnesia.*

a. In Salts of Magnesia with Organic or Volatile Inorganic Acids.

The salt of magnesia is gently heated in a covered platinum crucible, increasing the temperature gradually, until no more fumes escape; the lid is then removed, and the crucible placed in an oblique position, with the lid leaning against it. A red heat is now applied, until the residue is perfectly white. For the properties of the residue, see § 74. The method gives the more accurate results the more slowly the salt is heated from the beginning. Some loss of substance is usually sustained, owing to traces of the salt being carried off with the empyreumatic products. Salts of magnesia with readily volatile oxygen acids (carbonic acid, nitric acid), may be transformed into magnesia in a similar way, by simple ignition. Even sulphate of magnesia loses the whole of its sulphuric acid when exposed, in a platinum crucible, to the heat of the gas blowpipe-flame (SONNENSCHEIN). As regards small quantities of sulphate of magnesia, I can fully confirm this statement.

b. Conversion of Chloride of Magnesium into pure Magnesia. See § 153, 4, γ.

THIRD GROUP OF THE BASES.

ALUMINA—SESQUIOXIDE OF CHROMIUM—(TITANIC ACID).

§ 105.

1. ALUMINA.

a. Solution.

Those of the compounds of alumina which are insoluble in water, dissolve, for the most part, in hydrochloric acid. Native crystallized alumina (sapphire, ruby, corundum, &c.), and many native alumina compounds, and also artificially produced alumina after intense ignition, require fusing with carbonate of soda, caustic potassa, or hydrate of baryta, as a preliminary step to their solution in hydrochloric acid. Many alumina compounds which resist the action of concentrated hydrochloric acid, may be decomposed by protracted heating with moderately concentrated sulphuric acid, or by fusion with bisulphate of potassa; *e.g.*, common clay.

b. Determination.

Alumina is invariably weighed in the *pure state* (§ 75). The several compounds of alumina are converted into pure alumina, either by precipitation as hydrate of alumina, and subsequent ignition, or by simple ignition. Precipitation as basic acetate or basic formiate is resorted to only in cases of separation.

We may convert into

PURE ALUMINA.

a. By Precipitation.	*b. By Heating or Ignition.*
All compounds of alumina soluble in water, and those which, insoluble in that menstruum, dissolve in hydrochloric acid, with separation of their acid.	α. All salts of alumina with readily volatile acids (*e.g.*, nitrate of alumina). β. All salts of alumina with organic acids.

With regard to the method *a*, it must be remembered that the solution must contain no organic substances, which would interfere with the precipitation—*e.g.*, tartaric acid, sugar, &c. Should such be present, the solution must be mixed with carbonate of soda and nitrate of potassa, evaporated to dryness in a platinum dish, the residue fused, then softened with water, transferred to a beaker, digested with hydrochloric acid, and the solution filtered, and then, but not before, precipitated.

The methods *b*, α and β, are applicable only in cases where no other fixed substances are present. The methods of estimating alumina in its combinations with phosphoric, boracic, silicic, and chromic acids, will be found in Part II. of this Section, under the heads of these several acids.

Determination as pure Alumina.

a. By Precipitation.

Mix the moderately dilute hot solution of alumina, in a beaker or dish, with a tolerable quantity of chloride of ammonium, if that salt is not already present; add ammonia *slightly* in excess, boil gently till the steam ceases to brown turmeric paper, allow to settle; then decant the clear supernatant fluid on to a filter, taking care not to disturb the precipitate; pour boiling water on the latter in the beaker, stir, let the precipitate subside, decant again, and repeat this operation of washing by decantation a second and a third time; transfer the precipitate now to the filter, finish the washing with boiling water, dry thoroughly, ignite (§ 52), and weigh. The heat applied should be very gentle at first, and the crucible kept well covered, to guard against the risk of loss of substance from spirting, which is always to be apprehended if the precipitate is not *thoroughly* dry; towards the end of the process the heat should be raised to intense redness. In the case of *sulphate* of alumina the foregoing process is apt to leave some sulphuric acid in the precipitate, which, of course, vitiates the result. To insure the removal of this sulphuric acid, the precipitate should be exposed for 5–10 min. to the heat of the gas blowpipe flame. If there are difficulties in the way, preventing this proceeding, the precipitate, either simply washed or moderately ignited, must be re-dissolved in hydrochloric acid (which requires protracted warming with strong acid), and then precipitated again with ammonia; or the sulphate must first be converted into nitrate by decomposing it with nitrate of lead, added in very slight excess, the excess of lead removed by means of hydrosulphuric acid, and the further process conducted according to the directions of *a* or *b*. For the properties of hydrate of alumina and ignited alumina, see § 75. The method, if properly executed, gives very accurate results. But if a considerable excess of ammonia is used, more particularly in the absence of ammoniacal salts, and the liquid is filtered without boiling or long standing in a warm place to remove the ammonia, no trifling loss may be incurred. This loss is the greater, the more dilute the solution, and the larger the excess of ammonia. The precipitate cannot well be sufficiently washed on the filter on account of its gelatinous nature; on the other hand, if it be entirely washed by decantation, a very large quantity of wash-water must be used, hence it is advisable to combine the two methods, as directed.*

b. By Ignition.

α. Compounds of Alumina with Volatile Acids.

Ignite the salt (or the residue of the evaporated solution) in a platinum crucible, gently at first, then gradually to the very highest degree of intensity, until the weight remains constant. For the properties of the residue, see § 75. Its purity must be carefully tested. There are no sources of error.

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* [When a solution of alumina in hydrate of potassa or hydrate of soda is boiled with excess of chloride of ammonium, the alumina separates completely as a hydrate with two eq. of water, which may be washed with comparative ease. In certain cases, as where alumina is separated from sesquioxide of iron by hydrate of soda, this fact may be taken advantage of. Löwe, Fres. Zeitschrift, IV. 355.]

β. *Compounds of Alumina with Organic Acids.*

The same method as described § 104, 3, *a* (Magnesia).

§ 106.

2. SESQUIOXIDE OF CHROMIUM.

a. Solution.

Many of the compounds of sesquioxide of chromium are soluble in water. The hydrated sesquioxide, and most of the salts insoluble in water, dissolve in hydrochloric acid. Ignition renders sesquioxide of chromium and many of its salts insoluble in acids; this insoluble modification must be prepared for solution in hydrochloric acid, by fusing with 3 or 4 parts of potassa. A small quantity is converted, in the process of fusing, into chromic acid, by the action of the air; this is, however, reduced again to sesquioxide upon heating with hydrochloric acid. Addition of alcohol greatly promotes the reduction. Instead of this fusing with potassa, we frequently prefer to adopt a treatment, whereby the sesquioxide is at once oxidized and converted into an alkaline chromate (see 2). For the solution of chromic iron, see § 160.

b. Determination.

Sesquioxide of chromium is always, when directly determined, weighed in the *pure state*. It is brought into this form either by precipitation as hydrate and ignition, or by simple ignition. It may, however, also be estimated, by conversion into chromic acid, and determination as such.

We may convert into

1. PURE SESQUIOXIDE OF CHROMIUM.

a. By Precipitation.

All compounds of sesquioxide of chromium soluble in water, and also those which, insoluble in that menstruum, dissolve in hydrochloric acid, with separation of their acid. Provided always that no organic substances (such as tartaric acid, oxalic acid, &c.) which interfere with the precipitation be present.

b. By Ignition.

α. All salts of sesquioxide of chromium with volatile oxygen acids, provided no non-volatile substances be present.

β. Salts of sesquioxide of chromium with organic acids.

2. CHROMIC ACID, or, more correctly speaking, ALKALINE CHROMATE.

Sesquioxide of chromium and all its salts.

The methods of analyzing the combinations of the sesquioxide of chromium with chromic acid, phosphoric acid, boracic acid, and silicic acid, will be found in Part II. of this Section, under the heads of these several acids.

1. *Determination as Sesquioxide of Chromium.*

a. By Precipitation.

The solution, which must not be too highly concentrated, is heated to 100° in a beaker. Ammonia is then added slightly in excess, and the mixture exposed to a temperature approaching boiling, until the fluid over the precipitate is perfectly colorless, presenting no longer the least shade of red; let the solid particles subside, wash three times by decantation, and lastly on the filter, with hot water, dry thoroughly, and ignite (§ 52). The heat in the latter process must be increased gradually, and the crucible kept covered, otherwise some loss of substance is likely to arise from spirting upon the incandescence of the sesquioxide of chromium which marks the passing of the soluble into the insoluble modification. For the properties of the precipitate and residue, see § 76. This method, if properly executed, gives very accurate results.

b. By Ignition.

a. Salts of Sesquioxide of Chromium with Volatile Acids.

The same method as described, § 105, *b*, *α* (Alumina).

b. Salts of Sesquioxide of Chromium with Organic Acids.

The same method as described § 104, 3, *a* (Magnesia).

2. CONVERSION OF SESQUIOXIDE OF CHROMIUM INTO CHROMIC ACID.

(For the estimation of chromic acid, see § 130.)

The following methods have been proposed with this view:—

a. The solution of the salt of sesquioxide of chromium is mixed with solution of potassa or soda in excess, until the hydrated sesquioxide, which forms at first, is redissolved. Chlorine gas is then conducted into the cold fluid until it acquires a yellowish-red tint; it is then mixed with potassa or soda in excess, and the mixture evaporated to dryness; the residue is ignited in a platinum crucible. The whole of the chlorate of potassa (or soda) formed is decomposed by this process, and the residue consists, therefore, now of an alkaline chromate and chloride of potassium (or sodium).—(VOHL.)

b. Hydrate of potassa is heated in a silver crucible to calm fusion; the heat is then somewhat moderated, and the perfectly dry compound of sesquioxide of chromium projected into the crucible. When the sesquioxide of chromium is thoroughly moistened with the potassa, small lumps of fused chlorate of potassa are added. A lively effervescence ensues, from the escape of oxygen; at the same time the mass acquires a more and more yellow color, and finally becomes clear and transparent. Loss of substance must be carefully guarded against (H. SCHWARZ).

c. Dissolve the sesquioxide of chromium in solution of potassa or soda, add binoxide of lead in sufficient excess, and warm. The yellow fluid produced contains all the chromium as chromate of lead in alkaline solution. Filter from the excess of binoxide of lead, add to the filtrate acetic acid to acid reaction, and determine the weight of the precipitated chromate of lead (G. CHANCEL*).

[*d.* Render the solution of sesquioxide of chromium nearly neutral by a solution of carbonate of soda, add acetate of soda in excess, heat and add chlorine water, or pass in chlorine gas, keeping the solution nearly neutral by occasional addition of carbonate of soda. The oxidation proceeds readily. Boil off excess of chlorine, when the chromic acid may be precipitated as chromate of lead or chromate of baryta (W. Gibbs *).]

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* Comp. rend. 43, 927.

§ 107.

Supplement to the Third Group.

TITANIC ACID.

Titanic acid is always weighed in the pure state; its separation is effected either by precipitation with an alkali or by boiling its dilute acid solution. In *precipitating* acid solutions of titanic acid ammonia is employed; take care to add the precipitating agent only in slight excess, let the precipitate formed, which resembles hydrate of alumina, deposit, wash, first by decantation, then completely on the filter, dry, and ignite (§ 52). If the solution contained sulphuric acid, put some carbonate of ammonia into the crucible, after the first ignition, to secure the removal of every remaining trace of that acid. Lose no time in weighing the ignited titanic acid, as it is slightly hygroscopic. If we have titanic acid dissolved in sulphuric acid, as for instance occurs when we fuse it with bisulphate of potassa and treat the mass with cold water, we may, by largely diluting, and long boiling, with renewal of the evaporating water, fully precipitate the titanic acid. Thus separated, it is easy to wash. In the process of igniting the dried precipitate, some carbonate of ammonia is added. From dilute hydrochloric acid solutions of titanic acid, the latter separates completely only upon evaporating the fluid to dryness; and if the precipitate in that case were washed with pure water, the filtrate would be milky; acid must, therefore, be added to the water.

Hydrate of titanic acid precipitated in the cold, washed with cold water, and dried without elevation of temperature, is completely soluble in hydrochloric acid; otherwise it dissolves only incompletely in that acid. Titanic acid thrown down from dilute acid solutions by boiling, is not soluble in dilute acids. Ignited titanic acid does not dissolve even in concentrated hydrochloric acid, but it does dissolve by long heating with tolerably concentrated sulphuric acid. The easiest way of effecting its solution is to fuse it for some time with bisulphate of potassa, and treat the fused mass with a large quantity of cold water. Upon fusing with carbonate of soda, titanate of soda is formed, which, when treated with water, leaves acid titanate of soda, which is soluble in hydrochloric acid. Titanic acid ($Ti\ O_2$) consists of 60·98 per cent. of titanium, and 39·02 per cent. of oxygen.

FOURTH GROUP OF THE BASES.

OXIDE OF ZINC—PROTOXIDE OF MANGANESE—PROTOXIDE OF NICKEL—PROTOXIDE OF COBALT—PROTOXIDE OF IRON—SESQUIOXIDE OF IRON—(SESQUIOXIDE OF URANIUM).

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* [Am. Journ. Sci. 2 Ser. 39, 58.]

§ 108.

1. Oxide of Zinc.

a. Solution.

Many of the salts of zinc are soluble in water. Metallic zinc, oxide of zinc, and the salts, which are insoluble in water, dissolve in hydrochloric acid. To dissolve sulphide of zinc it is best to employ nitric acid or aqua regia.

b. Determination.

Zinc is weighed either as *oxide* or as *sulphide* (§ 77). The conversion of the salts of zinc into the oxide is effected either by precipitation as basic carbonate or sulphide of zinc, or by direct ignition. Besides these gravimetric methods, several volumetric methods are in use.

We may convert into

1. Oxide of Zinc.

a. By Precipitation as Carbonate of Zinc.

All the salts of zinc which are soluble in water, and all those with organic volatile acids; also those salts of zinc which, insoluble in water, dissolve in hydrochloric acid, with separation of their acid.

b. By Precipitation as Sulphide of Zinc.

All compounds of zinc without exception.

c. By direct Ignition.

Salts of zinc with volatile inorganic oxygen acids.

2. Sulphide of Zinc.

All compounds of zinc without exception.

The method 1, *c*, is to be recommended only, as regards the more frequently occurring compounds of zinc, for the carbonate and the nitrate. The methods 1, *b*, or 2, are usually only resorted to in cases where 1, *a*, is inadmissible. They serve more especially to separate oxide of zinc from other bases. Salts of zinc with organic acids cannot be converted into the oxide by ignition, since this process would cause the reduction and volatilization of a small portion of the metal. If the acids are volatile, the zinc may be determined at once, according to method 1, *a*: if, on the contrary, the acids are non-volatile, the zinc is best precipitated as sulphide. For the analysis of chromate, phosphate, borate, and silicate of zinc, look to the several acids. The volumetric methods are chiefly employed for technical purposes; see Special Part.

1. *Determination as Oxide of Zinc.*

a. By Precipitation as Carbonate of Zinc.

Heat the moderately dilute solution nearly to boiling in a *capacious* vessel, best in a platinum dish; add, drop by drop, carbonate of soda in excess; boil a few minutes; allow to subside, decant through a filter, and boil the precipitate three times with water, decanting each time; then transfer the precipitate to the filter, wash completely with hot water, dry, and ignite as directed § 53, taking care to have the filter as clean as practicable, before proceeding to incinerate it. Should the solution contain ammoniacal salts, the ebullition must be continued until, upon a fresh addition of the carbonate of soda, the escaping vapor no longer imparts a brown tint to turmeric paper. If the quantity of ammoniacal salts present is considerable, the fluid must be evaporated *boiling* to dryness. It is, therefore, in such cases more convenient to precipitate the zinc as sulphide (see *b*).

The presence of a great excess of acid in the solution of zinc must be as much as possible guarded against, that the effervescence from the escaping carbonic acid gas may not be too impetuous. The filtrate must always be tested with sulphide (with addition of chloride) of ammonium to ascertain whether the whole of the zinc has been precipitated; a *slight* precipitate will indeed *invariably* form upon the application of this test; but, if the process has been properly conducted, this is so insignificant that it may be altogether disregarded, being limited to some exceedingly slight and imponderable flakes, which moreover make their appearance only after many hours' standing. If the precipitate is more considerable, however, it must be treated as directed in *b*, and the weight of the oxide of zinc obtained added to that resulting from the first process. For the properties of the precipitate and residue, see § 77. This method yields pretty accurate results, though they are in most cases a little too low, as the precipitation is never *absolutely* complete, and as particles of the precipitate will always and unavoidably adhere to the filter, which exposes them to the chance of reduction and volatilization during the process of ignition. On the other hand, the results are sometimes too high; this is owing to defective washing, as may be seen from the alkaline reaction which the residue manifests in such cases. It is advisable also to ascertain whether the residue will dissolve in hydrochloric acid without leaving silicic acid; this latter precaution is indispensable in cases where the precipitation has been effected in a glass vessel.

[It is often better, especially in presence of ammonia salts, to heat the dry zinc salt with excess of carbonate of soda in a platinum dish cautiously to near redness, then treat with hot water and wash as directed.]

b. By Precipitation as Sulphide of Zinc.

Mix the solution, contained in a not too large flask and sufficiently diluted, with chloride of ammonium, then add ammonia, till the reaction is just alkaline, and then colorless or slightly yellow sulphide of ammonium in moderate excess. If the flask is not now quite full up to the neck, make it so with water, cork, allow to stand 12 to 24 hours in a warm place, wash the precipitate, if considerable, first by decantation, then on the filter with water containing sulphide of ammonium and also less and less chloride of ammonium (finally none). In decanting do not pour the fluid through the filter, but at once into a flask. After thrice decanting, filter the fluid that was poured off, and then transfer the precipitate to the filter, finishing the washing as directed. The funnel is kept covered with a glass plate. If the zinc is not to be determined according to 2, then put the moist filter with the precipitate in a beaker, and pour over it moderately dilute hydrochloric acid slightly in excess. Put the glass now in a warm place, until the solution smells no longer of sulphuretted hydrogen; dilute the fluid with a little water, filter, wash the original filter with hot water, and proceed with the solution of chloride of zinc obtained as directed in *a*.

From a solution of acetate of zinc the metal may be precipitated completely, or nearly so, with sulphuretted hydrogen gas, even in presence of an excess of acetic acid, provided always no other acid be present (Expt. No. 74). The precipitated sulphide of zinc is washed with water impregnated with sulphuretted hydrogen, and, for the rest, treated exactly like the sulphide of zinc obtained by precipitation with sulphide of ammonium.

Small quantities of sulphide of zinc may also be converted directly into the oxide, by heating in an open platinum crucible, to gentle redness at first, then, after some time, to most intense redness.

c. By direct Ignition.

The salt is exposed, in a covered platinum crucible, first to a gentle heat, finally to a most intense heat, until the weight of the residue remains constant. The action of reducing gases is to be avoided.

2. *Determination as Sulphide of Zinc.*

The precipitated sulphide of zinc, obtained as in 1, *b*, may be ignited in hydrogen and weighed. H. Rose,* who has lately recommended the process, employs the following apparatus.

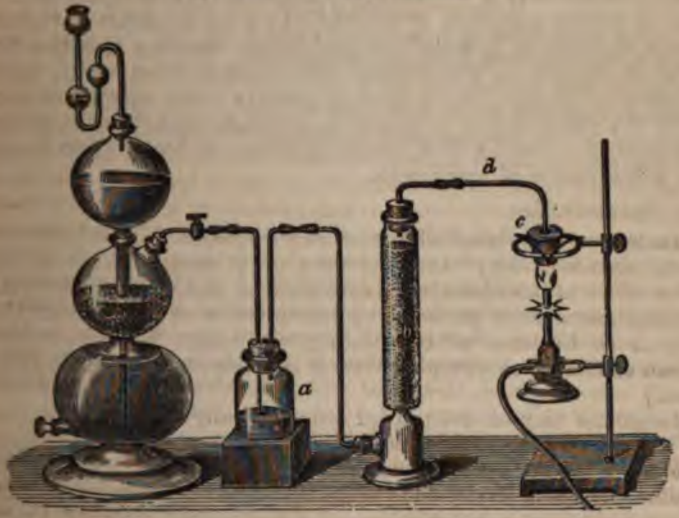

Fig. 47.

a contains concentrated sulphuric acid, *b*, chloride of calcium. The porcelain crucible has a perforated porcelain or platinum cover, into the opening of which fits the porcelain or platinum tube, *d*. The latter is provided with an annular projection which rests on the cover, the tube itself extends some distance into the crucible. When the sulphide of zinc has dried in the filter, it is transferred to the weighed porcelain crucible, the filter ashes added, powdered sulphur is sprinkled over the contents of the crucible, the cover is placed on, and hydrogen is passed in a moderate stream, a gentle heat is applied at first, which is afterwards raised for five minutes to intense redness; finally the crucible is allowed to cool with continued transmission of the gas, and the sulphide of zinc is weighed.

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* Pogg. Anal. 110, 128.

[Instead of the porcelain tube and perforated cover, a common tobacco-pipe may be employed, the bowl of the latter being inverted over or within a porcelain crucible. Sulphuretted hydrogen may be advantageously substituted for hydrogen.]

OESTEN's experiments, which were adduced by ROSE in support of the accuracy of this method, were highly satisfactory.

Sulphate, carbonate, and oxide of zinc may be converted into sulphide in the manner just described. They must, however, be mixed with an excess of powdered sulphur, otherwise you will lose some zinc from the reducing action of the hydrogen (H. ROSE).

§ 109.

2. PROTOXIDE OF MANGANESE.

a. Solution.

Many of the salts of protoxide of manganese are soluble in water. The pure protoxide, and those of its salts which are insoluble in that menstruum, dissolve in hydrochloric acid, which dissolves also the higher oxides of manganese. The solution of the higher oxides is attended with evolution of chlorine—equivalent in quantity to the amount of oxygen which the oxide under examination contains, more than the protoxide of manganese—and the fluid, after application of heat, is found to contain protochloride of manganese.

b. Determination.

Manganese is weighed either as *protosesquioxide*, as *sulphide*, or as *pyrophosphate* (§ 78.) Into the form of protosesquioxide it is converted either by precipitation as carbonate of protoxide, or as hydrated protoxide, sometimes preceded by precipitation as sulphide of manganese, or as binoxide of manganese; or, finally, by direct ignition. [When estimated as pyrophosphate it is precipitated as ammonio-phosphate.]

Manganese may be determined volumetrically in two different ways, one being applicable to any solution of protoxide of manganese, provided it be free from any other substance which exerts a reducing action on alkaline solution of ferricyanide of potassium, the other being only admissible, when we have manganese in the condition of a perfectly definite higher oxide, and free from other bodies, which evolve chlorine on boiling with hydrochloric acid.

We may convert into

1. PROTOSESQUIOXIDE OF MANGANESE.

a. By Precipitation as Carbonate of Protoxide of Manganese.

All the soluble salts of manganese with inorganic acids, and all its salts with volatile organic acids; also those of its salts which, insoluble in water, dissolve in hydrochloric acid with separation of their acid.

b. By Precipitation as Hydrated Protoxide of Manganese.

All the compounds of manganese, with the exception of its salts with non-volatile organic acids.

c. By Precipitation as Sulphide of Manganese.

All compounds of manganese without exception.

d. By Separation as Binoxide of Manganese.

All compounds of manganese in a slightly acid solution, especially acetate and nitrate of protoxide of manganese.

e. By direct Ignition.

All oxygen compounds of manganese; salts of manganese with readily volatile acids, and with organic acids.

2. Sulphide of Manganese.

All compounds of manganese without exception.

3. Pyrophosphate of Manganese.

All the oxides and many of the salts of manganese.

The method 1, *e*, is simple and accurate, but seldom admissible. The method 1, *a*, is the most usually employed; if one's choice is free, it is to be preferred to 1, *b*. The methods 1, *c*, and 2, are generally used, when the methods 1, *a*, or *b*, cannot be adopted—say on account of the presence of a non-volatile organic substance, and also when we have to separate manganese from other metals. The latter object may be attained also by the method 1, *d*. The process 3, is very convenient and accurate in absence of alkaline earth and heavy metals. The phosphate and borate of manganese are treated, either according to the method 1, *b*, as the salts precipitated from acid solution by potassa are completely decomposed upon boiling with excess of potassa, or according to the method 2. In silicates the manganese is determined after the separation of the silicic acid (§ 140), according to 1, *a*, or 3; for the analysis of chromate of protoxide of manganese, see § 130 (chromic acid). The volumetric method by reduction of ferricyanide of potassium is comparatively new, and especially suited for technical work, in which the highest degree of accuracy is not required. The estimation of manganese from the quantity of chlorine disengaged upon boiling the oxides with hydrochloric acid, is resorted to, more particularly, to determine the degrees of oxidation of manganese, and permits also the estimation of manganese in presence of other metals (see Section V).

1. *Determination as Protosesquioxide of Manganese.*

a. By Precipitation as Carbonate of Protoxide of Manganese.

The precipitation and washing are effected in exactly the same way as directed § 108, 1, *a* (determination of zinc as oxide, by precipitation as carbonate). If the filtrate is not absolutely clear, stand it in a warm place for twelve to twenty-four hours. A slight precipitate will then separate, which is collected on another small filter. The precipitate is dried, and then ignited as directed § 53. The lid is removed from the crucible, and a strong heat maintained until the weight of the residue remains constant. Care must be taken to prevent reducing gases finding their way into the crucible. For the properties of the precipitate and residue, see § 78. This method, if properly executed, gives accurate results. The principal point is to continue the application of a sufficiently intense heat long enough to effect the object in view. It is necessary also to ascertain whether the residue has not an alkaline reaction, and having removed it from the platinum crucible, whether it dissolves in hydrochloric acid without leaving silica.

b. By Precipitation as Hydrated Protoxide of Manganese.

The solution should not be too concentrated, and it is best to have it in a platinum dish. Precipitate with solution of pure soda or potassa, and proceed in all other respects as in *a.*

If phosphoric acid is present, or boracic acid, the fluid must be kept boiling for some time with an excess of alkali. For the properties of the precipitate, see § 78.

c. By Precipitation as Sulphide of Manganese.

The solution contained in a comparatively small flask and not too dilute is first mixed with chloride of ammonium (if an ammonia salt is not already present in sufficient quantity), then—if the fluid is acid—with ammonia, till it reacts neutral or very slightly alkaline; now add yellow sulphide of ammonium in moderate excess, if the flask is not already quite full up to the neck, add water till it is, cork, stand it in a warm place for at least twenty-four hours, wash the precipitate if at all considerable, first by decantation, then on the filter, using water containing sulphide of ammonium, and also gradually diminished quantities of chloride of ammonium (finally none). In decanting, pour the fluid in a flask, not on the filter. After decanting three times, filter the fluids that have been poured off, transfer the precipitate to the filter, and finish the washing as above directed, without interruption. Keep the funnel covered with a glass plate. If you do not prefer to determine according to 2, proceed as follows:—Put the moist filter with the precipitate into a beaker, add hydrochloric acid, and warm until the mixture smells no longer of sulphuretted hydrogen; filter, wash the residuary paper carefully, and precipitate the filtrate as directed in *a.* The results are satisfactory, compare § 78, *e.*

d. By Separation as Binoxide of Manganese.

Heat the solution of the acetate of protoxide of manganese or some other compound of the protoxide containing but little free acid, after addition of a sufficient quantity of acetate of soda, to from 50° to 60°, and transmit chlorine gas through the fluid. The whole of the manganese present falls down as binoxide (SCHIEL,—RIVOT, BEUDANT, and DAGUIN). Wash, first by decantation, then upon the filter; dry, transfer the precipitate to a flask, add the filter ash, heat with hydrochloric acid, filter, and precipitate as directed in *a.* If the acetate of soda is deficient, and especially if hydrochloric acid is present, it may happen that the precipitation of the manganese by chlorine is not quite complete; it is therefore well, after filtering off the peroxide, to treat the filtrate with more acetate of soda, and again pass chlorine. The separation of manganese as binoxide, by evaporating its solution in nitric acid to dryness, and heating the residue, finally to 155°, is given in Section V.

[Bromine may be most advantageously substituted for chlorine gas. When the quantity of binoxide is small it may be directly converted into protosesquioxide by intense ignition, as it retains but one or two per cent. of alkali. It may also be estimated as pyrophosphate, § 109, 3.

e. By direct Ignition.

The manganese compound under examination is introduced into a platinum crucible, which is kept closely covered at first, and exposed to a gentle heat; after a time the lid is taken off, and replaced loosely on the crucible, and the heat is increased to the highest degree of intensity, with careful exclusion of reducing gases; the process is continued until the weight of the residue remains constant. The conversion of the higher oxides of manganese into protosesquioxide of manganese requires more protracted and intense heating than the conversion of the protoxide. In fact, it can hardly be effected without the use of a gas blowpipe. In the case of salts of manganese with organic acids, care must always be taken to ascertain whether the whole of the carbon has been consumed; and should the contrary turn out to be the case, the residue must either be dissolved in hydrochloric acid, and the solution precipitated as directed in *a*, or 3 or it must be repeatedly evaporated with nitric acid, until the whole of the carbon is oxidized. The method, if properly executed, gives accurate results. On the other hand, if the directions are not carefully attended to, one must not be surprised at considerable differences. In the ignition of salts of manganese with organic acids, minute particles of the salt are generally carried away with the empyreumatic products evolved in the process, which, of course, tends to reduce the weight a little.

2. *Determination as Sulphide of Manganese.*

The sulphide precipitated as in 1, *c*, may be determined in this form, as follows: Dry, transfer the precipitate to a crucible, burn the filter, add the ashes, strew some sulphur on the top, ignite strongly in hydrogen (till it becomes black) and weigh as anhydrous sulphide of manganese (H. ROSE *), compare the analogous process for zinc, § 108, 2.

The results obtained by OESTEN, and cited by ROSE, are perfectly satisfactory.

This method is shorter and more convenient than dissolving the moist sulphide in hydrochloric acid, and precipitating with carbonate of soda.

The protosulphate and all the oxides of manganese may be subjected to this process with the same result.

[3. *Determination as Pyrophosphate of Manganese.*

To the solution of manganese, which may contain salts of ammonia or alkalies, phosphate of soda is added in large excess above what is needful to convert the manganese into phosphate. The white precipitate is then redissolved in sulphuric or chlorhydric acid, the liquid is heated to boiling, best in a platinum dish, and ammonia added in excess. The boiling is continued 10—15 minutes, whereby the white, semi-gelatinous precipitate first formed is converted into rose-colored, pearly scales. The whole is kept hot for an hour longer, then filtered and washed with hot water containing a little ammonia. The precipitate of ammonio-phosphate of manganese is dried, separated from the filter, and converted by ignition into pyrophosphate. Results accurate, see § 78 (GIBBS*, HENRY†).]

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* Pogg. Anal. 110, 122.

4. *Volumetric determination by the Reduction of Ferricyanide of Potassium* (E. LENSSEN‡).

The method is grounded on the fact that if a solution of protoxide of manganese which contains 1 eq. Fe_2O_3 to 1 eq. MnO, is acted on by excess of alkaline solution of ferricyanide of potassium at a boiling temperature, all the manganese is precipitated as binoxide, while a corresponding quantity of ferrocyanide of potassium is formed. By determining the latter, the amount of manganese present is obtained.

$$K_3\,Cfy_2 + 2\ KO + MnO,SO_3 = 2\ K_2\,Cfy + KO,SO_3 + MnO_2.$$

Accordingly 1 eq. manganese gives rise to 2 eq. ferrocyanide of potassium. Of course all other reducing substances must be absent, and the manganese must be present entirely in the form of proto-salt. If the solution contains no sesquioxide of iron, the precipitate is a combination of much binoxide, with little protoxide, not always in the same proportions. In performing the process, mix first with the acid solution of protoxide of manganese so much sesquichloride of iron that you may be sure of having at least 1 eq. Fe_2O_3 to 1 eq. MnO, and add the mixture gradually to a boiling solution of ferricyanide of potassium, previously rendered strongly alkaline with potassa or soda. After boiling together a short time the brownish-black precipitate becomes granular and less bulky. Allow to cool *completely*, filter off and wash the precipitate, acidify the filtrate with hydrochloric acid, and estimate the ferrocyanide of potassium with permanganate, according to § 147, II., *g.* *α.* If the liquid is filtered hot, the results are too high, as the filter in this case has a reducing action. The method may be shortened, as follows: After boiling, transfer the solution, together with the precipitate, to a measuring flask, allow to cool, fill up to the mark with water, shake, and allow to settle. Filter through a dry filter, take out a certain quantity with a pipette, and determine the ferrocyanide in this. A slight source of error is here introduced by disregarding the volume of the precipitate. The results adduced by LENSSEN are very satisfactory. I have myself repeatedly tested this method, and I have to remark as follows:—

a. If ferricyanide of potassium is long boiled with pure potassa, a small quantity of ferrocyanide is invariably produced.

b. The potassa must be quite free from organic substances, and should therefore, if there is any doubt on this point, be fused in a silver dish before use, otherwise the error alluded to in *a* may be considerably increased.

c. The complete washing of the voluminous precipitate is attended with so much difficulty and loss of time as to render the method more troublesome than a gravimetric analysis.

d. The abridged method, on the other hand, may be of great service in certain cases, especially when a series of manganese determinations have to be made, the manganese not being in too minute quantities, and the highest degree of accuracy not being required. In my laboratory, by employing a slight excess of sesquioxide of iron, 97·9—100·12—

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[*] Am. Jour. Sci. 2d Ser. 44. p. 216. [†] Am. Jour. Sci. 2d Ser., 47, p. 130.

[‡] Journ. f. prakt. Chem. 80, 408.

98·21—98·99, and 100·4 were obtained, instead of 100. The inaccuracy increases on using a large excess of the iron.*

5. *Volumetric determination by boiling the higher oxides with hydrochloric acid, and estimating the chlorine evolved.*

The methods here employed will be found all together in the Special Part under "Valuation of Manganese Ores."

§ 110.

3. Protoxide of Nickel.

a. Solution.

Many of the salts of protoxide of nickel are soluble in water. Those which are insoluble, as also the pure protoxide, in its common modification, dissolve, without exception, in hydrochloric acid. The peculiar modification of protoxide of nickel, discovered by Genth, which crystallizes in octahedra, does not dissolve in acids, but is rendered soluble by fusion with bisulphate of potassa. Metallic nickel dissolves slowly, with evolution of hydrogen gas, when warmed with dilute hydrochloric or sulphuric acid; in nitric acid, it dissolves with great readiness. Sulphide of nickel is but sparingly soluble in hydrochloric acid, but it dissolves readily in nitrohydrochloric acid. Peroxide of nickel dissolves in hydrochloric acid, upon the application of heat, to protochloride, with evolution of chlorine.

b. Determination.

Protoxide of nickel is always weighed as such (§ 79). The compounds of nickel are converted into the pure protoxide, usually by precipitation as hydrated protoxide, preceded, in some instances, by precipitation as sulphide of nickel, or by ignition.

We may convert into

PROTOXIDE OF NICKEL.

a. By Precipitation as Hydrated Protoxide or Sesquioxide of Nickel.	*b. By Precipitation as Sulphide of Nickel.*
All the salts of nickel with inorganic acids which are soluble in water, and all its salts with volatile organic acids; likewise all salts of nickel which, insoluble in water, dissolve in the stronger acids, with separation of their acid.	All compounds of nickel without exception.

c. By Ignition.

The salts of nickel with readily volatile oxygen acids, or with such oxygen acids as are decomposed at a high temperature (carbonic acid, nitric acid).

The method *c* is very good, but seldom admissible. The method *a* is most frequently employed. In the presence of sugar, or other non-volatile organic substance, it cannot be used. In this case we must either ignite and thereby destroy the organic matter before precipitating, or we must resort to the method *b*, which otherwise is hardly used except in separations. The combinations of the protoxide of nickel with chromic, phosphoric, boracic, and silicic acids are analyzed according to the methods given under the several acids.

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* Zeitschr. f. Anal. Chem. 3, 209.

Determination as Protoxide of Nickel.

a. By Precipitation as Hydrated Protoxide of Nickel.

Mix the solution with pure solution of potassa or soda in excess, heat for some time nearly to ebullition, decant 3 or 4 times, boiling up each time, filter, wash the precipitate *thoroughly* with hot water, dry and ignite *intensely* (RUSSELL *) (§ 53). The precipitation is best effected in a platinum dish; in presence of nitrohydrochloric acid, or, if the operator does not possess a sufficiently capacious dish of the metal, in a porcelain dish; glass vessels do not answer the purpose so well. Presence of ammoniacal salts, or of free ammonia, does not interfere with the precipitation. For the properties of the precipitate and residue, see § 79. This method, if properly executed, gives very accurate results. The thorough washing of the precipitate is a most essential point. It is necessary also to ascertain whether the residue has not an alkaline reaction, and whether it dissolves completely in hydrochloric acid.

[Addition of solution of hypochlorite of soda to the hot liquid, after treatment with caustic soda, converts the protoxide into *sesquioxide*, which washes more easily than the protoxide, and is otherwise treated like the latter.]

b. By Precipitation as Sulphide of Nickel.

This requires the greatest care and attention when sulphide of ammonium is employed.

α. The moderately dilute cold solution of nickel contained in a proper sized flask is, if necessary, neutralized with ammonia (the reaction should be rather slightly acid than alkaline): chloride of ammonium is added, if not already present in sufficient quantity, and then hydrosulphate of sulphide of ammonium, as long as a precipitate is produced. (The NH_4S, HS should be perfectly saturated with HS; it may be colorless or light-yellow.) A large excess of the reagent must be avoided. After mixing, fill the flask with water up to the neck, cork, and allow to stand about twenty-four hours without warming, but in a moderately warm place. The precipitate has now settled, and the clear supernatant fluid is colorless or slightly yellow. Decant, filter, and wash as described in the case of sulphide of manganese (§ 109, 1, *c*). (Filtrate and wash-water must be colorless or slightly yellow.) Dry the precipitate in the funnel, and transfer as completely as possible from the filter, to a beaker; the filter is incinerated in a coil of platinum wire, or upon the lid of a crucible, and the ash added to the dry precipitate. The precipitate is now treated with concentrated nitrohydrochloric acid, and the mixture digested at a gentle heat, until the whole of the sulphide of nickel is dissolved, and the undissolved sulphur appears of a pure yellow; the fluid is then diluted, filtered, and the filtrate precipitated, &c., as directed in *a*. For the properties of the precipitate, see § 79. The method, if properly executed, gives accurate results.

If the solution contains free ammonia, or no salt of ammonia, the fluid filtered off from the sulphide of nickel possesses always a more or less brownish tint, and contains sulphide of nickel (§ 79, *c*), which must be regained by acidifying with acetic acid and boiling. If the precipitate is not washed as directed, some nickel is very likely to pass through with the wash-water. If the filter were not incinerated, but treated at once, together with the precipitate, with nitrohydrochloric acid, the solution of the sulphide of nickel would contain organic substances, and the soda or potassa would accordingly afterwards fail to effect the complete precipitation of the nickel.

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* Journ. Chem. Soc. 16, 58.

β. Mix the slightly acidified solution of nickel with bicarbonate of ammonia, so that the free acid may be neutralized, and the solution may contain a small excess of the bicarbonate of ammonia, together with free carbonic acid, and then pass hydrosulphuric acid gas through the mixture. Precipitation will promptly ensue. Filter, and treat the precipitate as in α.

[γ. When a boiling solution of sulphide of sodium* is added to a boiling solution of a salt of nickel, sulphide of nickel is thrown down completely, and may be filtered and washed with hot water without the least oxidation. It is best to add some acetic acid before filtering, to destroy any excess of sulphide of sodium. (GIBBS.†)]

It is not advisable to convert the sulphide of nickel in Ni_2S, by igniting in hydrogen with addition of sulphur, and in this form to weigh it, as the composition of the residue is not quite constant. (H. ROSE.)

c. By direct Ignition.

The same method as described § 109, 1, *e*. (Manganese.)

§ 111.

4. PROTOXIDE OF COBALT.

a. Solution.

Protoxide of cobalt and its compounds behave with solvents like the corresponding compounds of nickel; metallic cobalt like metallic nickel. The protosesquioxide of cobalt obtained by SCHWARZENBERG in microscopic octahedra does not dissolve in boiling hydrochloric acid, or nitric acid, nor in nitrohydrochloric acid; but it dissolves in concentrated sulphuric acid, and in fusing bisulphate of potassa.

b. Determination.

Cobalt may be weighed as *metallic cobalt, protoxide of cobalt, sulphate of protoxide of cobalt*, and *nitrite of cobalt and potassa*. The conversion into protoxide is often preceded by precipitation as hydrated sesquioxide, and conversion into the sulphate by precipitation as sulphide of cobalt.

We may convert into

1. METALLIC COBALT.

All salts of cobalt that may be reduced directly by hydrogen gas (chloride of cobalt, nitrate of protoxide of cobalt, carbonate of protoxide of cobalt, &c.) and all the oxides.

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* [Pure sulphide of sodium may be procured by dissolving crystallized sulphide ($NaS, 9 HO$), in alcohol of 90 *per cent.* and recrystallizing two or three times from the solvent. The pure salt is dried in vacuo, and the white effloresced mass preserved in a well-stoppered bottle. (Gibbs.)]

[† Am. Jour. Sci. 2d Ser. 37, 350.]

2. Protoxide of Cobalt.

All salts of cobalt which are soluble in water, or in stronger acids, with separation of their acid, except those with non-volatile organic acids. Also all the higher oxides, and all salts whose acids are destroyed or expelled by ignition.

3. Sulphate of Protoxide of Cobalt.

All compounds of cobalt without exception.

4. Nitrite of Cobalt and Potassa.

All compounds of cobalt soluble in water or acetic acid.

1. *Determination as Metallic Cobalt.*

Evaporate the solution of chloride of cobalt, or of nitrate of protoxide of cobalt, which must be free from sulphuric acid and alkali, in a weighed crucible, to dryness; cover the crucible with a lid having a small aperture in the middle, conduct through this a moderate current of pure dry hydrogen gas, and then apply a gentle heat, which is to be increased gradually to intense redness. When the reduction is considered complete, let the reduced metal cool in the current of hydrogen gas, and weigh; ignite again in the same way and repeat the process until the weight of the reduced metal remains constant. The results are accurate. For the properties of cobalt, see § 80.

[The oxides of cobalt which have been precipitated by an alkali after ignition may be reduced in the same manner. The metal retains a small portion of alkali which may be removed by washing with hot water down to unweighable traces. Unless alkali absolutely free from silica, and platinum vessels be employed in the precipitation, the metal, after weighing, should be dissolved, the solution evaporated to dryness on the water-bath, that any residue of silica may be separated.]

As regards the apparatus to be employed, see fig. 47, p. 181.

[2. *Determination as Protoxide of Cobalt.*

a. By Precipitation as Hydrated Sesquioxide.

The solution is precipitated exactly as described for nickel, with solution of soda under addition of a hypochlorite. § 110, *a.* The precipitate is also further treated as there directed, with the important difference that the dried precipitate is ignited and cooled in a stream of pure carbonic acid gas until the weight remains constant. See § 80.

When precipitated as hydrated sesquioxide with reagents free from silica, &c., the precipitate retains but trifling traces of alkali, and the method is very accurate.

b. By Ignition.

Carbonate and nitrate of cobalt are ignited in a stream of carbonic acid as above. Organic salts are ignited in the air until carbon is burned off, and then in an atmosphere of carbonic acid.]

3. *Determination as Sulphate of Protoxide of Cobalt.*

a. By direct Conversion.

The solution is evaporated to dryness, in a platinum dish or platinum crucible*—(directly, if it contains sulphate of protoxide of cobalt; but if it contains a volatile acid, after addition of a slight excess of sulphuric acid)—and the residue cautiously heated, at a gradually increased temperature, which is finally raised to gentle redness: the application of heat is continued until no more fumes escape and the weight of the crucible remains constant. In order to avoid spirting while heating, it is well to hold the flame above the crucible, and let it play on the cover.

After weighing, the salt is treated with hot water. If this fails to effect complete solution (a sign that the salt has become basic) the residue is dissolved in hydrochloric acid, and the amount of sulphuric acid is then estimated in the solution, as directed § 132; the difference will be the protoxide of cobalt. The results are accurate.

For the properties of sulphate of protoxide of cobalt see § 80.

b. Preceded by Precipitation as Sulphide of Cobalt.

Precipitate, decant, filter and wash exactly as directed for sulphide of manganese (§ 109, 1, *c*), dry, and redissolve as directed § 110, *b*, *α* (Sulphide of nickel.)

The solution obtained contains invariably sulphuric acid; the amount of the cobalt is determined according to 3, *a*, taking care to evaporate the fluid, which contains nitrohydrochloric acid, in a porcelain dish, with addition of sulphuric acid, to dryness, before transferring the residue, with a little water, to the platinum dish. The results are accurate.

For the properties of the sulphide of cobalt see § 80. The sulphide of cobalt cannot be brought into a weighable form by ignition in hydrogen, as the residue is a variable mixture of different sulphides (H. Rose).

4. *Determination as Nitrite of Cobalt and Potassa* (used principally in cases of separation).

Mix the cobalt solution, which must not be too dilute (at the most, 300 parts of water to 1 of protoxide of cobalt), with a concentrated solution of nitrite of potassa; add acetic acid in quantity, a little more than sufficient to redissolve the precipitate, which is at first produced in the solution by the free potassa and carbonate of potassa contained in the nitrite. Cover the beaker with a clock-glass, and let it stand 12 to 24 hours in a warm place. Collect the yellow precipitate on a weighed filter, wash thoroughly with an aqueous solution of neutral acetate of potassa (containing 10 per cent. of the salt), to which some nitrite of potassa is added, displace, finally, the last portion of solution of acetate of potassa still adhering to the precipitate, by means of spirit of wine of 80 per cent., dry, ignite, incinerate the filter, moisten the whole with sulphuric acid, drive off the excess of the latter (see § 97, 1), and weigh the residue which consists of $2\,(Co\,O,\,S\,O_3) + 3\,(K\,O,\,S\,O_3)$. Gibbs and Genth † have obtained good results by this method.

100 parts of the residue are equivalent to 18·014 parts of Co O.

[Or dissolve the nitrite of cobalt and potassa in hydrochloric acid, precipitate by potassa, reduce the washed precipitate by hydrogen, and weigh the washed metal. (H. Rose.)]

[To weigh the precipitate dried at 100° is not recommended, since Erdmann has shown that its content of water and nitrogen is variable. See § 80.]

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[*] The operation must, at all events, be *finished* in a platinum vessel.

[†] Annal. d. Chem. u. Pharm. 104, 309.

§ 112.

5. Protoxide of Iron.

a. Solution.

Many of the compounds of protoxide of iron are soluble in water. The compounds insoluble in water dissolve almost without exception in hydrochloric acid, in which the pure protoxide also is soluble; the solutions, if not prepared with perfect exclusion of air, and with solvents absolutely free from air, contain invariably more or less sesquichloride. In cases where it is wished to avoid the chance of oxidation, the solution of the compound of protoxide of iron is effected in a small flask, through which a slow current of carbonic acid gas is passed, the transmission of the gas being continued until the solution is cold. Many native proto-compounds of iron cannot be thus dissolved. They are, indeed, rendered soluble by fusing with carbonate of soda, but in this process the protoxide of iron is converted into sesquioxide It is therefore advisable to heat such substances (in the finest powder) with a mixture of 3 parts concentrated sulphuric acid and 1 part water in a strong sealed tube of Bohemian glass for 2 hours at about 210°, or—in the case of silicates—to warm them with a mixture of 2 parts hydrochloric acid and 1 part strong hydrofluoric acid in a covered platinum dish (A. Mitscherlich *. See also Cooke's method of solution, p. —). Metallic iron dissolves in hydrochloric acid, and in dilute sulphuric acid, with evolution of hydrogen, as protochloride or sulphate of protoxide respectively; in warm nitric acid it dissolves as nitrate of sesquioxide, and in nitro-hydrochloric acid as sesquichloride.

b. Determination.

Protoxide of iron may be estimated 1, by dissolving, converting into sesquioxide and determining the latter gravimetrically or volumetrically; 2, by precipitating as sulphide, and weighing it as such, or determining it after conversion into sesquioxide; 3, by a direct volumetric method; 4, by treating with terchloride of gold, and weighing the reduced gold.

The methods 1 and 2 are, of course, only applicable when no sesquioxide is present with the protoxide; the method 2 is scarcely ever used except for separations. The methods included under 3 are adapted to most cases and, in absence of other reducing substances, are especially worthy of recommendation. The method 4 will be briefly treated of in the supplement to §§ 112 and 113.

As the determination of iron as sesquioxide belongs to § 113, and as the process for precipitating the protoxide as sulphide is the same as that for precipitating the sesquioxide in this form, nothing remains for us here but to describe the methods of converting the protoxide into the sesquioxide and the processes included under 3.

1. *Methods of converting Protoxide of Iron into Sesquioxide.*

a. Methods, applicable in all cases.

Heat the solution of protoxide of iron to be oxidized with hydrochloric acid and add small portions of chlorate of potassa, till the fluid, even after warming for some time, still smells strongly of chlorine. Our object may be also attained by passing chlorine gas or—in the case of small quantities—by addition of chlorine water. If the solution is required to be free from excess of chlorine, it is finally heated, till all odor of that gas has disappeared.

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* Journ. f. prakt. Chem. 81, 116.

b. Methods which are only suitable when the iron is to be subsequently precipitated by ammonia, as hydrated sesquioxide.

Mix the solution of the protoxide of iron in a flask with a little hydrochloric acid, if it does not already contain any; add some nitric acid, and heat the mixture for some time to incipient ebullition. The color of the fluid will show whether the nitric acid has been added in sufficient quantity. Though an excess of nitric acid does no harm, still it is better to avoid adding too much on account of the subsequent precipitation. In concentrated solutions, the addition of nitric acid produces a dark-brown color, which disappears upon heating. This color is owing to the nitric oxide formed dissolving in the still unoxidized portion of the solution of the protoxide.

c. Methods which can be employed only when the sesquioxide of iron is to be determined volumetrically.

Add to the hydrochloric solution small quantities of artificially prepared iron-free binoxide of manganese, till the solution is of a dark olive green color from the formation of sesquichloride of manganese; boil till this coloration and the odor of chlorine have disappeared (FR. MOHR); or you may add pure permanganate of potassa (in crystals or concentrated solution) till the fluid is just red and then boil, till the red color and chlorine-odor have vanished. These methods present the advantage of permitting complete oxidation without the use of any considerable excess of the oxidizing agent.

2. *Estimation by Volumetric Analysis.*

a. MARGUERITE'S *Method.*

This method is based upon the following principle:—

If we add to a solution of protoxide of iron, containing an excess of sulphuric acid, permanganate of potassa, the former is oxidized at the expense of the latter [$10\ (Fe\,O, S\,O_3) + 8\ S\,O_3 + K\,O, Mn_2O_7 = 5\ (Fe_2\,O_3, 3\ S\,O_3) + K\,O, S\,O_3 + 2\ (Mn\,O, S\,O_3)$]. Now if we possess a solution of permanganate of potassa, and know how much iron 100 c. c. of it can convert from the condition of protoxide to that of sesquioxide, we can, with this, readily determine an unknown quantity of iron; we have simply, for this purpose, to dissolve the iron in acid, in the form of protoxide, to oxidize the solution accurately, and note how many c. c. of the solution of permanganate of potassa have been used to accomplish that object.

α. Determination of the Strength of the Solution of Permanganate of Potassa.

The process of preparing a solution of permanganate of potassa having been described already in § 65, 3, I will at once proceed to give the several methods employed to determine the strength of the solution.

Either of the three subjoined methods may be selected for the purpose; or, the strength having been determined by one method, it may, by way of control, be determined once more by one of the other methods.

Solution of permanganate of potassa prepared from the pure crystallized salt, does not alter, if carefully kept; on the contrary, if it contains free potassa or manganate of potassa, it suffers gradual decomposition, and each analysis, made after an interval of even only a day, must be preceded by a fresh determination of its strength.

aa. Determination of the Strength by means of Metallic Iron.

Weigh off accurately about 0·2 grm. of thin, clean iron wire (pianoforte wire); introduce this into a small long-necked flask, add about 20 c. c. of dilute sulphuric acid, and the same quantity of water, secure the flask in an oblique position, by means of a retort-holder; transmit through it a slow current of carbonic acid, and then heat the fluid to gentle ebullition.

Fig. 48 shows the arrangement of the apparatus. When the iron has dissolved, allow to cool, keeping up the current of carbonic acid, then fill the flask two-thirds with distilled water; smear the rim with a little tallow, pour the contents cautiously into a beaker of about 400 c. c. capacity, and transfer the last particles from the flask to the beaker by repeated rinsing with cold water. The total quantity of fluid should be about 200 c. c. Place the beaker on a sheet of white paper, or better, on a sheet of glass, with white paper underneath.

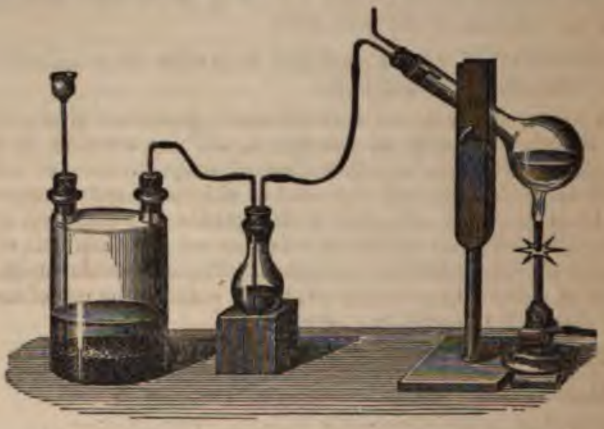

Fig. 48.

Fill a GAY-LUSSAC's or GEISSLER's burette of 30 c. c. capacity, divided into $\frac{1}{10}$ c. c. (see §§ 22, 23, figs. 13 and 14), up to zero, with solution of permanganate of potassa, of which take care to have ready a sufficient quantity, perfectly clear and uniformly mixed.

Now add the permanganate to the iron solution, stirring the latter all the while with a glass rod. At first the red drops disappear very rapidly, then more slowly. The fluid, which at first was nearly colorless, gradually acquires a yellowish tint. From the instant the red drops begin to disappear more slowly, add the permanganate with more caution and in single drops, until the last drop imparts to the fluid a faint, but unmistakable reddish color, which remains on stirring. A little practice will enable you readily to hit the right point. As soon as the fluid in the burette has sufficiently collected again, read off, and mark the number of c. c. used. The reading off must be performed with the greatest exactness (see § 22); the whole error should not amount to $\frac{1}{10}$ c. c.

If 0·2 grm. iron have taken from 20 to 30 c. c. of permanganate, the latter may be considered to be of the proper degree of concentration for most determinations of iron. If much less has been used in the process, the solution is too concentrated. In that case add to the entire quantity a sufficient amount of water to give it approximately the right degree of concentration; then repeat the above experiment with a fresh amount of iron. If, on the other hand, considerably more than 30 c. c. of permanganate have been used for 0·2 grm. iron, the solution is not exactly unfit for use, but working with it becomes the more tedious and inconvenient the more its degree of concentration differs from that given above.

When you have completed the experiment with a solution of approximately proper concentration, calculate, by a simple proportion, how much iron 100 c. c. of the solution will convert from the state of protoxide to that of sesquioxide. Supposing, for instance, you have used to 0·210 grm. iron, 23·5 c. c. of the permanganate, then we say

$$23{\cdot}5 : 100 :: 0{\cdot}210 : x \qquad x = 0{\cdot}8936 \text{ (grm. iron)}.$$

As the accuracy of all estimations made with the solution of permanganate of potassa depends upon the correct determination of the strength, it is always advisable to repeat the experiment.

As even the purest iron wire is not chemically pure, but contains a little carbon, it is well, in analyses requiring the very highest degree of accuracy, to reduce the weight of the iron wire used in the process, by multiplication with 0·997, to the corresponding weight of chemically pure iron. This reduction is based upon the generally correct supposition that the wire contains 0·3 per cent. of extraneous matter.

If, in the two experiments made for the purpose of determining the strength of the solution of permanganate of potassa, the quantities of iron respectively corresponding to 100 c. c. of solution, differ only about 1, 2, or 3 mgrm. (per grm.), the results may be considered perfectly satisfactory. But if the difference is considerably greater, a third experiment must be made.

If there is a deficiency of free acid in the solution of iron, the fluid acquires a brown color, turns turbid, and deposits a brown precipitate (binoxide of manganese and sesquioxide of iron). The same may happen also if the solution of permanganate of potassa is added too quickly, or if the proper stirring of the iron solution is omitted or interrupted. Experiments attended with abnormal manifestations of the kind should always be rejected. That the fluid reddened by the last drop of solution of permanganate of potassa added, loses its color again after a time, need create no surprise or uneasiness; this decolorization is, in fact, quite inevitable, as a dilute solution of free permanganic acid cannot keep long undecomposed.

bb. Determination of the Strength by means of Sulphate of Protoxide of Iron and Ammonia.

Weigh off, with the greatest accuracy, about 1·4 grm. of the pure salt prepared according to the directions given in § 65, 4, after powdering the crystals, and pressing between sheets of smooth blotting-paper. Dissolve in about 200 c. c. distilled water, add about 20 c. c. dilute sulphuric acid, and proceed as in *aa*.

As sulphate of protoxide of iron and ammonia contains exactly $\frac{1}{7}$ of its weight of iron, the calculation required to show the value of 100 c. c. of permanganate is very simple. Supposing, for instance, 25 c. c. of permanganate to have been consumed to 1·400 grm. of the iron salt, then,

we have $\frac{1{\cdot}4}{7} = 0{\cdot}2$

and $25 : 100 :: 0{\cdot}2 : x;$ $x = 0{\cdot}8$

If the sulphate of protoxide of iron and ammonia used is not pure, if, for instance, it contains bases isomorphous with protoxide of iron (protoxide of manganese, magnesia, &c.); or if it contains sesquioxide, or is used in a moist condition, the result will of course be too high.

cc. Determination of the Strength by means of Oxalic Acid.

This method is based upon the following principle:—

If solution of permanganate of potassa is added to a warm solution of oxalic acid, mixed with sulphuric acid, the liberated permanganic acid instantly oxidizes the oxalic acid to carbonic acid [$5\ C_2\ O_3 + 3\ S\ O_3 + K\ O,\ Mn_2\ O_7 = 10\ C\ O_2 + 2\ (Mn\ O,\ S\ O_3) + K\ O,\ S\ O_3$]. For the oxidation of 1 eq. oxalic acid ($C_2\ O_3$) and 2 eq. iron (in the state of protoxide) equal quantities of permanganic acid are accordingly required; therefore, 63 parts (1 eq.) of crystallized oxalic acid correspond, in reference to the oxidizing action of permanganic acid, to 56 parts (2 eq.) of iron.

By dissolving 6·3 grm. pure crystallized oxalic acid (§ 65, 1), or 4·5 grm. of the pure hydrate, dried at 100°, in water, to 1 litre of fluid, a decinormal solution of oxalic acid is obtained, which is exactly suited to our present purpose. 50 c. c. of this solution, which correspond to 0·315 grm. crystallized oxalic acid, or 0·28 grms. iron, are introduced into a beaker, diluted with about 100 c. c. of water, from 6 to 8 c. c. of conc. sulphuric acid added, and the fluid heated to about 60°. The beaker is then placed on a sheet of white paper, and permanganate added from the burette, with stirring. The red drops do not disappear at first very rapidly, but when once the reaction has fairly set in, they continue for some time to vanish instantaneously. As soon as the red drops begin to disappear more slowly, the solution of permanganate of potassa must be added with great caution; if proper care is taken in this respect, it is easy to complete the reaction with a single drop of permanganate; this completion of the reaction is indicated with beautiful distinctness in the colorless fluid. The number of c. c. used corresponds to 0·28 grm. iron.

If the oxalic acid was not perfectly dry, or not quite pure, the result of the experiment will, of course, lead to fixing the strength of the solution of permanganate of potassa too high. Instead of pure oxalic acid, SAINT-GILLES has proposed to use crystallized oxalate of ammonia ($N\ H_4\ O,\ C_2\ O_3 + aq.$). This can easily be prepared in the pure state, keeps well, and can be weighed with accuracy. It is not however advisable to keep a standard solution of this salt in store, as it is liable to spoil. 71 parts of the crystallized salt correspond to 56 parts iron.

Of the foregoing three methods of standardizing solution of permanganate of potassa, the first is the one originally proposed by MARGUERITE. Sulphate of protoxide of iron and ammonia was first proposed by FR. MOHR, and oxalic acid by HEMPEL, as agents suitable for the purpose. With absolutely pure and thoroughly dry reagents, and proper attention, all three methods give correct results.

For myself, I prefer the first method, as the most direct and positive, the only doubtful point about it being the question whether the assumption that the iron wire contains 99·7 per cent. of chemically pure iron is quite correct; this, however, is of very trifling importance, as the error could not exceed $\frac{1}{10}$ or $\frac{2}{10}$ per cent. But the other two methods are, as may readily be seen, somewhat more convenient, since in one of them the trouble is saved of preparing the solution of iron, and in the other there is, moreover, no need of weighing. These advantages, however, which were considerable when the impure permanganate solution that was used required fresh standardizing every day, have now lost their value, as the pure solution, now generally employed, keeps unaltered.

For the analysis of very dilute solutions of iron, *e.g.*, chalybeate water, in which the amount of iron may be very approximately determined with great expedition, by direct oxidization with permanganate, a very dilute standard solution must be prepared; of which 100 c. c. correspond to say 0·1 grm. iron. Such a solution should be directly standardized with correspondingly small quantities of iron, or the iron-double-salt, and boiled water should be used.

In experiments of this kind, the fact that a certain quantity of permanganate is required to impart a distinct color to pure acidified water (which is of no consequence in operations where the concentrated solution is used) must be taken into consideration; for where the solution used is so highly dilute, it takes indeed a measurable quantity of it to impart the desired reddish tint to the amount of water employed. In such cases, the volume of the solution of iron used for standardizing the permanganate and the volume of the weak ferruginous solution subjected to analysis should be the same, and either the two solutions should contain about the same quantity of iron, or, by means of a special experiment, it is ascertained how many $\frac{1}{10}$ c. c. of the permanganate are required to impart the desired pale red color to the same volume of acidified water. In the latter case, these $\frac{1}{10}$ c. c. will be deducted from the amount of permanganate used in the regular experiments.

β. *Performance of the Analytical Process.*

This has been fully indicated in α. The compound to be examined is dissolved, preferably with application of a current of carbonic acid (see fig. 48, p. 194), in water, or dilute sulphuric acid, allowed to cool in the current of carbonic acid, and suitably diluted (if practicable, the solution of a substance containing about 0·2 grm. iron should be diluted to about 200 c. c.); if free acid is not yet present in sufficient quantity, about 20 c. c. of dilute sulphuric acid are added, and then standard permanganate from the burette, to incipient reddening of the fluid. The volume of standard solution used is then read off. The strength of the solution of permanganate being known, the quantity of iron present in the examined fluid is found by a very simple calculation. Suppose 100 c. c. of solution of permanganate of potassa to correspond to 0·98 grm. iron, and 25 c. c. of the solution to have been used to effect the oxidation of the protoxide of iron in the examined compound; then

$$100 : 25 :: 0{\cdot}98 : x;\ x = 0{\cdot}245.$$

The quantity of iron originally present in the form of protoxide amounted accordingly to 0·245 grm.

For the method of determining the total amount of iron present in a solution containing both protoxide and sesquioxide of that metal, I refer to § 113; for that of determining the amount of each separately, to Section V.

NOTE ON THE DETERMINATION OF IRON IN HYDROCHLORIC ACID SOLUTION BY THE FOREGOING METHOD.

The foregoing process was long considered to be the most convenient and best for the estimation of iron. LÖWENTHAL and LENSSEN* have shown that in solutions containing *hydrochloric acid*, it is essential that the standardizing of the reagent and the actual analysis be performed under the same circumstances as regards dilution, amount of acid, and temperature. Besides the proper reaction $10\ Fe\ O + Mn_2\ O_7 = 5\ Fe_2\ O_3 + 2\ Mn\ O$, the collateral reaction $7\ H\ Cl + Mn_2\ O_7 = 5\ Cl + 2\ Mn\ Cl + 7\ H\ O$ also takes place, in consequence of which a little chlorine is liberated. This chlorine does not oxidize the protoxide of iron in the case of considerable dilution, but there occurs a condition of equilibrium in the fluid containing protoxide of iron, chlorine, and hydrochloric acid, which is destroyed by addition of a further quantity of either body (LÖWENTHAL and LENSSEN, *loc. cit.*). But since it is difficult to preserve the above condition of obtaining correct results, the following proceeding is adopted, *in presence of chlorine.*

Standardize the permanganate by means of iron dissolved in dilute sulphuric acid, make the iron solution to be tested up to ¼ litre, add 50 c. c. to a large quantity of water acidified with sulphuric acid, add permanganate from burette, then again 50 c. c. of the iron solution, permanganate again, &c., &c. The numbers obtained at the third and fourth time are taken. These are constant, while that obtained the first time, and sometimes also the second time, differs. The result multiplied by 5 gives exactly the quantity of permanganate proportional to the amount of protoxide of iron present.

I believe that the reason why the attention of analysts was not previously directed to the important influence of hydrochloric acid in this process, lay in the fact that it was not customary to crystallize the permanganate before employing it—the crude solution, which contains much chloride of potassium, being used. The experiments were consequently performed in the presence of free hydrochloric acid, even when sulphuric acid alone was employed for dissolving or acidifying. Hence the differences between the results with sulphuric and hydrochloric acid solutions were not so large as they are now, when we work with the pure permanganate.

b. PENNY'S *Method* (recommended subsequently by SCHABUS).

If bichromate of potassa is added to a strongly acid solution of protoxide of iron, the latter is converted into sesquioxide, whilst the chromic acid is reduced to sesquioxide of chromium ($6\ Fe\ O + 2\ Cr\ O_3 = 3\ Fe_2\ O_3 + Cr_2\ O_3$).

Now, with 0·1 eq. bichromate of potassa=14·759 grm. dissolved to 1 litre of fluid, 0·6 eq.=16·8 grm. iron may be converted from the state of protoxide to that of sesquioxide, and 50 c. c. of the above solution correspond accordingly to 0·84 grm. iron.

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* Zeitschrift f. analyt. Chem. 1, 329. See also 361.

Care must be taken to use perfectly pure bichromate of potassa; the salt is heated in a porcelain crucible until it is just fused; it is then allowed to cool under the desiccator, and the required quantity weighed off when cold. Besides the above solution, another should also be prepared, ten times more dilute, and containing accordingly 0·01 eq. of bichromate of potassa in the litre.

It is always advisable to test the correctness of the standard solution of bichromate of potassa, by oxidizing with it a known amount of pure iron dissolved to protoxide (see p. 194, *aa*).

The analytical process is performed as follows:—

The solution of protoxide of iron is sufficiently diluted, mixed with a sufficient quantity of hydrochloric or dilute sulphuric acid, and the standard solution of bichromate of potassa slowly added from the burette, the liquid being stirred all the while with a thin glass rod. The fluid, which is at first nearly colorless, speedily acquires a pale green tint, which changes gradually to a darker chrome-green. A very small drop of the mixture is now from time to time taken out by means of the stirring-rod, and brought into contact with a drop of a solution of ferricyanide of potassium on a porcelain plate, which has been spotted with several of such drops. When the blue color thereby produced begins to lose the intensity which it exhibited on the first trials, and to assume a paler tint, the addition of the solution of bichromate of potassa must be more carefully regulated than at first, and towards the end of the process a fresh essay must be made, and with larger drops than at first, after each new addition of two drops, and finally, even of a single drop; drops must also be left for some time in contact before the observation is taken. When no further blue coloration ensues, the oxidation is terminated. From the remarkable sensitiveness of the reaction, the exact point may be easily hit to a drop. To heighten the accuracy of the results, the dilute (ten times weaker) standard fluid should, just at the end of the process, be substituted for the concentrated solution of bichromate of potassa.

If exactly 0·84 grm. of the substance to be analyzed have been dissolved, the numbers of half c. c. used of the two standard fluids show how many per cents. and tenths per cent. respectively of pure iron the analyzed substance contains in the form of protoxide. For the manner of proceeding in presence of sesquioxide of iron, I refer to § 113. If there is a deficiency of free acid in the solution, brown chromate of sesquioxide of chromium may form, upon which the solution of protoxide of iron exercises no longer a deoxidizing action.

§ 113.

6. SESQUIOXIDE OF IRON.

a. Solution.

Many of the compounds of sesquioxide of iron are soluble in water. Pure sesquioxide of iron and most of those of its compounds which are insoluble in water, dissolve in hydrochloric acid, but many of them only slowly and with difficulty; compounds of this nature are best dissolved in concentrated hydrochloric acid, in a flask, with the aid of heat; which, however, should not be allowed to reach the boiling-point; the compound must, moreover, be finely powdered, and even then it will often take many hours to effect complete solution. Iron ores insoluble in hydrochloric acid are treated like the corresponding compounds of protoxide of iron [best by fusion with carbonate of soda].

b. Determination.

Sesquioxide of iron is usually weighed as such, but sometimes as sulphide (§ 81). It may, however, be estimated also indirectly, and also by volumetric analysis, both directly and after reduction to protoxide. The conversion of compounds of iron into sesquioxide is effected either by precipitation as hydrated sesquioxide, preceded in some cases by precipitation as sulphide of iron, or as succinate or basic acetate or basic formiate of sesquioxide of iron; or by ignition. While the volumetric and the now seldom-used indirect methods are applicable in almost all cases, we may convert into

1. SESQUIOXIDE OF IRON.

a. By Precipitation as Hydrated Sesquioxide.

All salts soluble in water with inorganic or volatile organic acids, and likewise those which, insoluble in water, dissolve in hydrochloric acid, with separation of their acid.

b. By Precipitation as Sulphide of Iron.

All compounds of iron without exception.

c. By Precipitation as Succinate of Sesquioxide of Iron; and

d. By Precipitation as Basic Acetate or Formiate of Sesquioxide of Iron.

The compounds enumerated sub *a.*

e. By Ignition.

All salts of sesquioxide of iron with volatile oxygen acids.

2. SULPHIDE OF IRON.

All compounds of iron without exception.

The method 1, *e*, is the most expeditious and accurate, and is therefore preferred in all cases where its application is admissible. The method 1, *a*, is the most generally used. The methods 1, *b*, and 2, serve principally to effect the separation of the sesquioxide of iron from other bases; they are resorted to also in certain instances where *a* is inapplicable, especially in cases where sugar or other non-volatile organic substances are present; and also to estimate the sesquioxide of iron in its compounds with phosphoric acid and boracic acid. The methods 1, *c* and 1, *d* are used exclusively in separations. For the manner of determining the sesquioxide of iron in the chromate and silicate, I refer to §§ 130 and 140. The volumetric methods for estimating the sesquioxide are used in technical experiments almost to the exclusion of all others, and are very frequently employed in scientific analyses.

1. *Determination as Sesquioxide of Iron.*

a. By Precipitation as Hydrated Sesquioxide.

Mix the solution in a dish or beaker with ammonia in excess, heat nearly to boiling, decant repeatedly on to a filter, wash the precipitate *carefully* with hot water, dry *thoroughly* (which very greatly reduces the bulk of the precipitate), and ignite in the manner directed in § 53.

For the properties of the precipitate and residue, see § 81. The method is free from sources of error. The precipitate, under all circumstances, even if there are no fixed bodies to be washed out, must be most *carefully* and *thoroughly* washed, since, should it retain any traces of chloride of ammonium, a portion of the iron would volatilize in the form of sesquichloride. It is also highly advisable to dissolve the weighed residue, or a portion of it, in strong hydrochloric acid, to see whether it is quite free from silicic acid.

b. By Precipitation as Sulphide of Iron.

The solution, in a not too large flask, is mixed with ammonia, till all the free acid is neutralized. (In the absence of organic, non-volatile substances this leads to the precipitation of a little hydrated sesquioxide, which, however, is of no consequence.) Add chloride of ammonium, if not already present in sufficient quantity, then colorless or yellowish sulphide of ammonium in moderate excess, lastly water, till the fluid reaches to the neck of the flask. Cork it up and stand in a warm place till the precipitate has subsided, and the supernatant fluid has a clear yellowish appearance (without a tinge of green). Wash as directed in the case of sulphide of manganese (§ 109, 1, *c*). Neglect of any of these precautions will occasion some loss of substance, the sulphide of iron gradually combining with the oxygen of the air, and passing thus into the filtrate as protosulphate. As this sulphate is reprecipitated by the sulphide of ammonium present, the filtrate assumes, in such cases, a greenish color, and gradually deposits a black precipitate, the separation of which is highly promoted by addition of chloride of ammonium. [See remarks in [ ] § 81, 5, c. p. 122.]

When the operation of washing is completed, the moist precipitate (if it is not dried and determined according to 2) is put, together with the filter, into a beaker, some water added, and then hydrochloric acid, until the whole is redissolved. Heat is now applied, until the solution smells no longer of sulphuretted hydrogen; the fluid is then filtered into a flask, the residual paper carefully washed, and the filtrate oxidized by heating with nitric acid (see § 112, 1); the oxidized solution is finally precipitated with ammonia, as in *a*.

If a solution of potassio-, sodio-, or ammonio-tartrate of sesquioxide of iron contains a considerable excess of alkaline carbonate, the precipitation of the iron as sulphide is prevented to a greater or less extent (BLUMENAU). In such cases the fluid must therefore be nearly neutralized with an acid, before the precipitation with the sulphide of ammonium can be effected.

c. By Precipitation as Succinate of Sesquioxide of Iron.

The solution, in a flask, is mixed with very dilute ammonia, drop by drop, until a small portion of the iron precipitates in the form of hydrated sesquioxide; a gentle heat is then applied, to ascertain whether or not the precipitate will redissolve. If it redissolves, the addition of dilute ammonia is continued, until the application of heat fails to redissolve the precipitate formed. If it remains undissolved, and the fluid still exhibits a brownish red color, all the preliminary conditions requisite for precipitation with succinate of ammonia are fulfilled. But should the fluid appear colorless, this is a sign that too much ammonia has been added; in which case it will be necessary to add a small portion of hydrochloric acid, and then again some ammonia, until the desired point is attained. To the fluid thus prepared is now added a perfectly neutral solution of succinate of ammonia, as long as a precipitate forms; a gentle heat is then applied, and the fluid allowed to cool; when perfectly cold it is filtered, and the precipitate washed, first with cold water, finally with warm ammonia—which operation, depriving the precipitate in a very great measure of its acid, imparts a darker tint to it. The washed precipitate is dried upon the filter in the funnel, and then converted into sesquioxide of iron, by ignition (§ 53). The object of washing the precipitate with ammonia is to remove part of the acid, since, were the precipitate simply washed with water, a portion of the sesquioxide of iron might suffer reduction upon the subsequent ignition of the succinate. If there is reason to apprehend that this has actually taken place, some nitric acid is added to the precipitate, evaporated, and the ignition repeated. For the properties of the precipitate, see § 81. The results are accurate.

d. By Precipitation as Basic Acetate of Sesquioxide of Iron.

Mix the solution of sesquioxide of iron [containing not more than 1 grm. of oxide to ½ litre] in a flask, if it contains much free acid, with carbonate of soda or ammonia until the acid is nearly neutralized; then add to the solution which is still clear, but already of a deep red color, neutral acetate of soda or of ammonia, and a few drops of acetic acid in slight excess; and boil till, on removing the lamp, the precipitate settles clear. Wash repeatedly by boiling and decantation, and finally on the filter with boiling water, which should contain a little acetate of ammonia; dry, ignite (§ 53), and weigh the sesquioxide obtained. It is advisable to add a few drops of nitric acid to the residue, evaporate, and ignite again, to see whether the weight remains constant. The residue must show no alkaline reaction when moistened with water. The results are accurate. It is often preferable to dissolve the precipitate of the basic acetate in hydrochloric acid, and to precipitate the solution according to *a* [see also Reichardt's method], § 81, *e*. The formiates of soda and ammonia may be advantageously substituted for the acetates as precipitants (§ 81, *f*).

e. By Ignition.

Expose the compound, in a covered crucible, to a gentle heat at first, and gradually to the highest degree of intensity; continue the operation until the weight of the residuary sesquioxide of iron remains constant.

2. *Determination as Anhydrous Sulphide of Iron.*

The hydrated sulphide of iron obtained, as in 1, *b*, may be very conveniently determined by conversion into the anhydrous sulphide. The process is the same as for zinc (§ 108, 2). The heat to which it is finally exposed in the current of hydrogen must be strong, as an excess of sulphur is retained with some obstinacy. In fact, it is advisable after weighing to re-ignite in hydrogen and weigh a second time. It is of no importance if the hydrated sulphide has oxidized on drying.

Protosulphate and sesquioxide of iron can be transformed into sulphide in the same manner, after having been dehydrated by ignition in a porcelain crucible (H. ROSE *).

The results obtained by OESTEN, and adduced by ROSE, as well as those obtained in my own laboratory, are exceedingly satisfactory. (Expt. No. 75.)

3. *Determination by Volumetric Analysis.*

a. Preceded by Reduction of the Sesquioxide to Protoxide.

The volumetric methods which come under this head are based upon the reduction of the sesquioxide to protoxide, and the estimation of the latter. We have, accordingly, to occupy ourselves simply with the reduction of the solution of the sesquioxide, the other part of the process having been fully discussed in § 112 (Protoxide of Iron). The reduction of sesquioxide of iron can be effected by many substances (zinc, protochloride of tin, sulphuretted hydrogen, sulphurous acid, &c.), but only those can be used with advantage, an excess of which may be added with impunity. If an excess must be very carefully avoided, or, being added, must be carefully removed, the method becomes troublesome, and a ready source of inaccuracy is introduced. On these grounds, although its action is somewhat slow, zinc, unquestionably, deserves the preference before all other reducing agents.

Heat the hydrochloric or sulphuric acid solution, which must contain a moderate excess of acid, but be free from nitric acid, in a small long-necked flask, placed in a slanting position; drop in small pieces of iron-free zinc (§ 60), and conduct a slow current of carbonic acid through the flask (fig. 48, p. 194). Evolution of hydrogen gas begins at once, and the color of the solution becomes paler in proportion as the sesquioxide changes to protoxide. Apply a moderate heat, to promote the action; and add also, if necessary, a little more zinc. As soon as the hot solution is completely decolorized (one cannot judge of the perfect deoxidation of a cold solution so well, as the color of the sesquichloride of iron is deeper in the heat), allow to cool completely in the stream of carbonic acid; to hasten the cooling the flask may be immersed in cold water; then dilute the contents with water, pour off and wash carefully into a beaker, leaving behind any undissolved zinc, and also (as far as possible) any flocks of lead that may have separated from the zinc, and proceed as directed in § 112, 2. If the solution contains metals precipitable by zinc, these will separate, and may render filtration necessary. In this case the filtrate must be again heated with zinc before using the standard solution. If iron-free zinc cannot be procured, the percentage of iron in the metal used must be determined, and weighed portions of it employed in the process of reduction; the known amount of iron contained in the zinc consumed is then subtracted from the total amount of iron found.

[*b. Without Previous Reduction to Protoxide.* OUDEMANS' *Method.*†

The principle consists in adding a reducing agent to the solution till the sesquioxide is entirely converted into protoxide, and then determining the amount of the reducing agent used.

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[*] Pogg. Annal. 110, 126.

[†] Fresenius' Zeitschrift, VI. 129.

This method depends upon the fact that hyposulphite of soda may reduce sesquioxide of iron to protoxide in accordance with the equation $Fe_2\,Cl_3 + 2\,(Na\,O, S_2\,O_2) = 2\,Fe\,Cl + Na\,O,\,S_4\,O_5 + Na\,Cl$. In order that this reaction serve for analytical purposes it is necessary, 1, that a certain—not too great—proportion of free acid be present; 2, that the iron solution be rather concentrated; and, 3, that a minute amount of solution of a salt of protoxide of copper be present, which acts to transfer oxygen from the iron to the hyposulphite, being reduced by the latter to suboxide and carried again to protoxide by the sesquisalt of iron. We require:—

a. A Solution of Hyposulphite of Soda.

This may be made by dissolving 25 grm. of the purest commercial salt in 1 litre of water.

b. A Standard Solution of a Sesquisalt of Iron.

This is prepared by dissolving 5·617 grm. of fine piano-wire, assumed to contain 99·7 per cent. of iron, in hydrochloric acid in a slanting long-necked flask, oxidizing the solution with chlorate of potassa, removing the excess of chlorine by protracted gentle boiling, and finally diluting the solution to 1 litre; or by dissolving 24·1 grm. of pure ammonia-iron-alum (see p. 93) in 1 litre of water.

c. A Solution of Sulphate of Copper containing, say, 10 per cent. of the crystallized salt.

d. A Solution of Sulphocyanide of Potassium.

The standard of the hyposulphite-solution must be fixed by aid of the accurately prepared iron-solution, as follows:—

20 c. c. of the iron-solution are measured into a small flask or beaker, well acidified with hydrochloric acid; one drop of the copper solution is added, and enough sulphocyanide to make the liquid of a deep red color. The hyposulphite (about 20 c. c.) is added from a burette, rapidly at first, afterwards slowly and cautiously, until the red color is discharged. The iron-solution may be warmed to 40° C. whereby the reaction is accelerated.

When the iron-solution is dilute, the reaction proceeds with inconvenient slowness, but after some practice the results are good. From the number of c. c. of the hyposulphite solution required to reduce a known quantity of sesquioxide of iron, taking the mean of a number of nearly accordant observations, may be calculated the quantity of sesquioxide of iron, or of metallic iron, corresponding to 1 c. c. of hyposulphite, and this factor, multiplied into the number of c. c. consumed in any analysis, gives the quantity of sesquioxide of iron or of metallic iron sought.

The solution of the iron which it is desired to estimate is conducted as described for making the standard *b*. It must be free from nitric acid and oxides of chlorine; should be kept rather concentrated, as a matter of convenience for rapid working, and should contain a moderate amount of free hydrochloric acid. The analysis is conducted as just described for the standardizing.

The solution of hyposulphite alters slowly with deposition of sulphur, and its value must be determined anew every week or two.

The process is convenient and excellent, though not so good for the estimation of minute quantities of iron as the method with permanganate.]

§ 114.

Supplement to the Fourth Group.

7. Sesquioxide of Uranium.

If the compound in which the sesquioxide of uranium is to be determined contains no other fixed substances, it may often be converted into *protosesquioxide* ($Ur\,O, Ur_2\,O_3$) by simple ignition. If sulphuric acid is present, small portions of carbonate of ammonia must be thrown into the crucible towards the end of the operation.

In cases where the application of this method is inadmissible, the solution of uranium (which, if it contains protoxide, must first be warmed with nitric acid, until the protoxide is converted into sesquioxide) is precipitated with ammonia. The yellow precipitate formed, which consists of hydrated *ammonio-sesquioxide of uranium*, is washed with a dilute solution of chloride of ammonium, to prevent the fluid passing milky through the filter. The precipitate is dried and ignited (§ 53). To make quite sure of obtaining the protosesquioxide in the pure state, the crucible is ignited for some time in a slanting position and uncovered; the lid is then put on, while the ignition is still continuing; the crucible is allowed to cool under the desiccator, and weighed (H. Rose).

If the solution from which the sesquioxide of uranium is to be precipitated contains other bases (alkaline earths, or even alkalies), portions of these will precipitate along with the ammonio-sesquioxide of uranium. For the measures to be resorted to in such cases, I refer to Section V.

The reduction of the protosesquioxide of uranium to the state of protoxide ($Ur\,O$) is an excellent means of ascertaining its purity for the purpose of control. This reduction is effected by ignition in a current of hydrogen gas, in the way described § 111, 1 (Cobalt). By intense ignition, the property of the protoxide of uranium to ignite in the air is destroyed. The separation of sesquioxide of uranium from phosphoric acid is effected by fusing the compound with cyanide of potassium and carbonate of soda. Upon extracting the fused mass with water, the phosphoric acid is obtained in solution, whilst the uranium is left as protoxide. Knop and Arendt * have employed this method.

The equivalent of protosesquioxide of uranium = 210·2, viz., 178·2 of uranium and 32 of oxygen. In 100 parts, the compound consists of 84·77 of uranium and 15·23 of oxygen. The equivalent of protoxide of uranium is 67·4, viz., 59·4 of uranium and 8 of oxygen; in 100 parts, the protoxide consists of 88·13 of uranium and 11·87 of oxygen.

FIFTH GROUP.

OXIDE OF SILVER—OXIDE OF LEAD—SUBOXIDE OF MERCURY—OXIDE OF MERCURY—OXIDE OF COPPER—TEROXIDE OF BISMUTH—OXIDE OF CADMIUM—(PROTOXIDE OF PALLADIUM).

§ 115.

1. Oxide of Silver.

a. Solution.

Metallic silver, and those of its compounds which are insoluble in water are best dissolved in nitric acid (if soluble in that acid). Dilute nitric acid suffices for most compounds; sulphide of silver, however, requires concentrated acid. The solution is effected best in a flask. Chloride, bromide, and iodide of silver are insoluble in water and in nitric acid. To get the silver contained in them in solution, proceed as follows:—fuse the salt in a porcelain crucible (this operation, though not absolutely indispensable, had better not be omitted), pour water over it, put a piece of clean zinc or iron upon it, and add some dilute sulphuric acid. Wash the reduced spongy silver, first with dilute sulphuric acid, then with water, and finally dissolve it in nitric acid. However, as we shall see below, the quantitative analysis of these salts does not necessarily involve their solution.

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* Chem. Centralbl. 1856, 773.

b. Determination.

Silver may be weighed as *chloride*, *sulphide*, or *cyanide*, or in the *metallic* state (§ 82). It is also frequently determined by volumetric analysis.

We may convert into

1. Chloride of Silver.

All compounds of silver without exception.

2. Sulphide of Silver. 3. Cyanide of Silver.

All compounds soluble in water or nitric acid.

4. Metallic Silver.

Oxide of silver, and some of its compounds with readily volatile acids; salts of silver with organic acids; chloride, bromide, iodide, and sulphide of silver.

The method 4 is the most convenient, and is preferred to the others in all cases where its application is admissible. The method 1 is that most generally resorted to. 2 and 3 serve mostly only to effect the separation of oxide of silver from other bases.

In assays for the Mint, silver is usually determined volumetrically by Gay-Lussac's method. Pisani's volumetric method is especially suited to the determination of very small quantities of silver. The estimation of silver by cupellation will be described in the Special Part.

1. *Determination of Silver as Chloride.*

a. In the Wet Way.

The precipitated chloride of silver may be separated from the supernatant fluid either by decantation or by filtration; the former is generally preferred for large quantities of precipitate, the latter answers better for small quantities. Whichever process is adopted, the chloride of silver must be completely protected from the influence of direct sunlight, and even the action of diffused daylight must be as far as possible avoided.

α. Determination by Decantation.

The moderately dilute silver-solution is introduced into a tall flask with long neck and narrow mouth, and some nitric acid added to it; the fluid is heated to about 60°, and hydrochloric acid carefully added in such quantity, that some silver still remains unprecipitated, and the chloride separates in consequence in large flocks. After their formation has been completed by gently moving the fluid, add cautiously more hydrochloric acid, till the last drops give no further precipitate (a considerable excess should be avoided, as hydrochloric acid dissolves very small traces of chloride of silver). The mouth of the flask is then closed with a perfectly smooth cork (or, better still, with a well-ground glass stopper), and the flask vigorously shaken until the precipitated chloride of silver has united into coherent lumps, and the supernatant fluid has become pretty clear. The chloride adhering to the neck of the flask is then removed by agitating the clear fluid, and the last traces are washed down by means of a wash-bottle; the flask is then allowed to stand at rest for twelve hours in a dark place at the ordinary temperature. At the end of this time the precipitate will have completely subsided and the fluid will be clear. The latter is then slowly and cautiously decanted, as far as practicable, into a beaker, so as to retain every particle of the chloride in the flask, whence it is carefully transferred to an upright smooth porcelain crucible that has been weighed: the last particles of chloride of silver are got out by putting a little water in the flask, closing the mouth with the finger, inverting, and rinsing the sides and bottom by agitation. The particles thus collect in the neck, and can easily be transferred to the crucible, by holding the mouth of the flask close over the latter, and letting the fluid run out; a washing bottle with the jet turned upwards (§ 46) may also be used with advantage.

When the chloride of silver has completely subsided in the crucible, which is greatly accelerated by exposure to the heat of a water-bath, the clear supernatant fluid is carefully decanted down a glass rod into the same beaker which contains the liquid of the first decantation. The chloride of silver in the crucible is moistened with a few drops of nitric acid, and then treated with hot distilled water; the chloride is again allowed to subside, the clear supernatant fluid again decanted, and the same operation repeated until a drop of the last decanted fluid no longer gives the slightest turbidity with nitrate of silver. The supernatant fluid is then removed as completely as possible by means of a pipette, or by cautious decantation; the chloride is thoroughly dried on the water-bath, and subsequently heated to incipient fusion over the lamp, taking care to apply a very gentle heat at first; as soon as the chloride begins to fuse round the border, the crucible is allowed to cool, and weighed.

To remove the mass from the crucible, completely and without injury to the latter, a piece of iron or zinc is placed upon the chloride, and highly dilute hydrochloric or sulphuric acid added. The crucible is finally cleansed, dried, and weighed, if this has not been done before the operation. Should the liquids successively decanted from the chloride of silver not be perfectly clear and transparent, they are kept standing in the cold until the last particles of chloride have completely subsided, which frequently requires many hours; the clear supernatant fluid is then decanted, and the deposited chloride added to the bulk of the precipitate in the crucible, the whole washed and treated as above; or—and this is a more expeditious way—the minute quantity of chloride is collected on a small filter, treated as directed in β, and added to the principal amount.

β. *Determination by Filtration.*

The chloride of silver is precipitated and allowed to subside as in α; the supernatant fluid is then passed through a small filter, to which the precipitate is subsequently transferred, with the aid of a little hot water acidulated with nitric acid; the precipitate collected on the filter is washed, first with water acidulated with nitric acid, afterwards with pure water; it is then thoroughly dried, the contents of the filter are transferred as completely as possible to a small porcelain crucible, and the filter itself is burnt on the lid. In this operation some of the chloride is always reduced, the ash is therefore added to the chloride in the crucible, together with two or three drops of dilute nitric acid: heat is applied for a short time, and then a drop or two of hydrochloric acid added; lastly heat, at first gently till dry, then to incipient fusion, and weigh.

For the properties of the precipitate, see § 82. Both methods give very accurate results, unless large quantities of such salts are present as have the property of slightly dissolving chloride of silver, compare § 82. In order to be quite safe in this connection it is advisable to test the clear filtrate with sulphuretted hydrogen before throwing it away.

b. In the Dry Way.

This method serves more exclusively for the analysis of bromide and iodide of silver, although it can be applied in the case of other compounds.

The process is conducted in the apparatus illustrated by Fig. 49, leaving off the tubes E and F, and employing a straight bulb-tube or a plain tube with porcelain tray instead of the bent tube D.

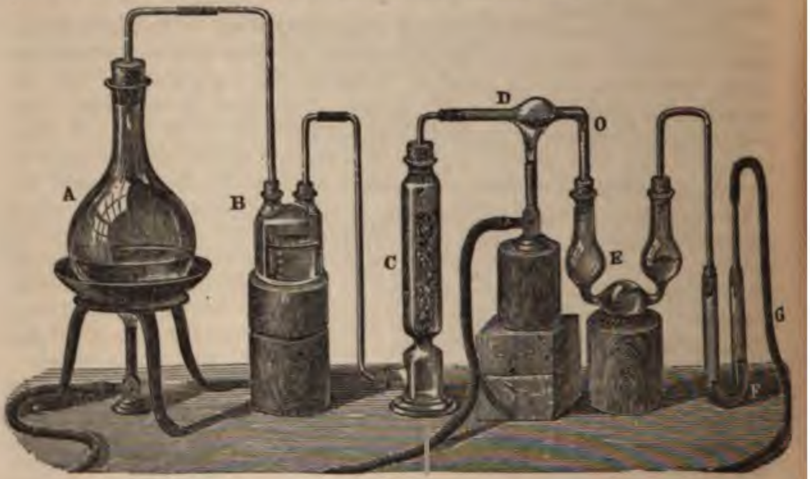

Fig. 49.

A is an apparatus for disengaging chlorine; B contains concentrated sulphuric acid, C chloride of calcium; D is a bulb-tube intended for the reception of the iodide or bromide of silver; and G, which directly is connected with D, serves to conduct the chlorine gas into the open air or into milk of lime. The operation is commenced by introducing the compound to be analyzed into the bulb, and applying heat to the latter until its contents are fused; when cold, the tube is weighed and connected with the apparatus. Chlorine gas is then evolved from A; when the evolution of the gas has proceeded for some time, the contents of the bulb are heated to fusion, and kept in this state for about fifteen minutes, agitating now and then the fused mass. The bulb-tube is then removed from the apparatus, allowed to cool, and held in a slanting position to replace the chlorine by atmospheric air; it is subsequently weighed, then again connected with the apparatus, and the former pro—

cess repeated, keeping the contents of D in a state of fusion for a few minutes. The operation may, in ordinary cases, be considered concluded if the weight of the tube suffers no variation by the repetition of the process. If the highest degree of accuracy is to be attained, heat the chloride of silver again to fusion, passing at the same time a slow stream of pure, dry carbonic acid through the tube, in order to drive out the traces of chlorine absorbed by the fused chloride. Allow to cool, hold obliquely for a short time, so as to replace the carbonic acid by air, and finally weigh. See § 82.

2. *Determination as Sulphide of Silver.*

Sulphuretted hydrogen precipitates silver conpletely from acid, neutral, and alkaline solutions; sulphide of ammonium precipitates it from neutral and alkaline solutions. Recently prepared perfectly clear solution of sulphuretted hydrogen may be employed to precipitate small quantities of silver; to precipitate larger quantities, the solution of the salt of silver (which must not be too acid) is moderately diluted, and washed sulphuretted hydrogen gas conducted into it. After complete precipitation has been effected, and the sulphide of silver has perfectly subsided (with exclusion of air), it is collected on a weighed filter, washed, dried at 100° and weighed. For the properties of the precipitate, see § 82. This method, if properly executed, gives very accurate results. The operator must take care to filter quickly, and to prevent the access of air as much as possible during the filtration, since, if this precaution be neglected, sulphur is likely to separate from the sulphuretted hydrogen water, which, of course, would add falsely to the weight of the sulphide of silver.

The sulphide of silver must, however, never be weighed as just described, unless the analyst is satisfied that no sulphur has fallen down with it, as would occur if the fluid contained hyponitric acid, sesquioxide of iron, or any other substance which decomposes sulphuretted hydrogen. In case the precipitate does contain admixed sulphur, the simplest process is to convert it into metallic silver (H. ROSE [*]). For this purpose it is transferred to a weighed porcelain crucible, the filter ash is added, and the whole is heated to redness in a stream of hydrogen, the apparatus described in § 108 being employed. Results accurate.

Should the apparatus in question not be at the operator's disposal, he may, after complete washing of the precipitate, carefully rinse it into a porcelain dish (without injuring the weighed filter), heat it once or twice with a moderately strong solution of pure sulphite of soda, re-transfer the precipitate (now freed from admixed sulphur) to the old filter, wash well, dry and weigh (J. LÖWE [†]); or he may treat the dried precipitate, together with the filter-ash, with moderately dilute chlorine-free nitric acid at a gentle heat, till complete decomposition has been effected (till the undissolved sulphur has a clean yellow appearance), filter, wash well, and proceed according to 1.

3. *Determination as Cyanide of Silver.*

Mix the neutral or acid solution of silver with cyanide of potassium, until the precipitate of cyanide of silver which forms at first is redissolved; add nitric acid in slight excess, and apply a gentle heat. After some time, collect the precipitated cyanide of silver on a weighed filter, wash, dry at 100°, and weigh. For the properties of the precipitate, see § 82. The results are accurate.

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[*] Pogg. Annal. 110, 139.

[†] Journ. f. prakt. Chem. 77, 73.

4. *Determination as Metallic Silver.*

Oxide of silver, carbonate of silver, &c., are easily reduced by simple ignition in a porcelain crucible. In the reduction of salts of silver with organic acids, the crucible is kept covered at first, and a moderate heat applied; after a time the lid is removed, and the heat increased, until the whole of the carbon is consumed. For the properties of the residue, see § 82. The results are absolutely accurate, except as regards salts of silver with organic acids; in the analysis of the latter, it not unfrequently happens that the reduced silver contains a minute portion of carbon, which increases the weight of the residue to a trifling extent.

If it is desired to transform chloride, bromide, iodide, or sulphide of silver into metallic silver, for the purpose of analysis, they are heated in a current of pure dry hydrogen to redness, till the weight remains constant. The process may be conducted in a porcelain crucible or a bulb-tube. In the former case, the apparatus described § 108, fig. No. 47 is used; in the latter the apparatus represented p. 208, with the substitution, of course, of hydrogen for chlorine. If the bulb-tube is used, it must, after cooling and before being weighed, be held in an inclined position, so that the hydrogen may be replaced by air. The results are perfectly accurate. See also Cupellation, Special Part.

5. *Volumetric Methods.*

1. Gay-Lussac's.

This, the most exact of all known volumetric processes, was introduced by Gay-Lussac as a substitute for the assay of silver by cupellation, was thoroughly investigated by him, and will be found fully described in his work on the subject. This method has been rendered still more precise by the researches of G. J. Mulder, to whose exhaustive monograph * I refer the special student of this branch. I shall here confine myself to giving the process so far as to suit the requirements of the chemical laboratory, taking only for granted that the analyst has the ordinary measuring apparatus, &c., at his disposal. Mulder's results will be made use of to the full extent possible under these circumstances.

a. Requisites.

α. Solution of chloride of sodium.

Take chemically pure chloride of sodium—either artificially prepared or pure rock-salt—powder it roughly and ignite moderately (not to fusion †).

Now dissolve 5·4145 grm. in distilled water to 1 litre, measured at 16°. 100 c. c. of this solution contains a quantity of chloride of sodium, equivalent to 1 grm. of silver.

The solution is kept in a stoppered bottle and shaken before use.

β. Decimal solution of chloride of sodium.

Transfer 50 c. c. of the solution described in α to a 500 c. c. measuring flask, fill up to the mark with distilled water and shake. Each c. c. of this decimal solution corresponds to 0·001 grm. silver. The measuring must be performed at 16°.

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* Die Silberprobirmethode (see note, p. 122).

† On fusion, if the flame can in the least way act upon it, it takes an alkaline reaction, since under the influence of vapor of water and carbonic acid, a little hydrochloric acid is formed and escapes, while a corresponding quantity of carbonate of soda remains.

The solution is kept as the other.

γ. Decimal silver solution.

Dissolve 0·5 grm. chemically pure silver in 2 to 3 c. c. pure nitric acid of 1·2 sp. gr., and dilute the solution with water exactly to 500 c. c. measured at 16°. Each c. c. contains 0·001 grm. silver. The solution is kept in a stoppered bottle and protected against the influence of light.

δ. Test-bottles.

These should be of white glass, holding easily 200 c. c., closed with well-ground glass stoppers, running to a point below. The bottles fit into cases blackened on the inside, and reaching up to their necks. In order to protect the latter also from the action of light, a black-cloth cover is employed.

b. Principle.

Suppose we know the value of a solution of chloride of sodium, *i.e.*, the quantity that is necessary to precipitate a given amount of silver, say 1 grm., we are in the position, with the aid of this solution, to determine an unknown amount of silver, for if we put x for the unknown amount of silver, then

c. c. of solution used for 1 grm. : c. c. used for x :: 1 grm. : x.

But if we examine whether 1 eq. chloride of sodium dissolved in water actually precipitates 1 eq. of silver dissolved in nitric acid exactly, we find that this is not the case. On the contrary, the clear supernatant fluid gives a small precipitate both on the addition of a little solution of chloride of sodium, and on the addition of a little silver-solution, as Mulder has most accurately determined. The value of a solution of chloride of sodium in the sense explained above cannot, therefore, be reckoned from the amount of salt it contains, by calculating 1 eq. silver for 1 eq. chloride of sodium, but it can only be obtained by experiment. Mulder has shown, that the temperature and the degree of dilution have some influence, and also that this fact is to be explained on the ground of the solvent power of the nitrate of soda produced on the chloride of silver. In the solution thus formed we have to imagine $Na\,O, N\,O_5$ and $Na\,Cl$ with $Ag\,O, N\,O_5$ in a certain state of equilibrium, which, on the addition of either $Na\,Cl$ or $Ag\,O, N\,O_5$ is destroyed, chloride of silver being precipitated.

From this interesting observation it follows, that if to a silver-solution we add at first concentrated solution of chloride of sodium, then decimal solution drop by drop, till the exact point is reached when no more precipitate appears, now, on addition of decimal silver-solution a small precipitate will be again produced; and if we add the latter drop by drop, till the last drop occasions no turbidity, then again decimal solution of chloride of sodium will give a small precipitate. On noticing the number of drops of both decimal solutions which are required to pass from one limit to the other, we find that the same number of each are used. Let us suppose that we had added decimal solution of chloride of sodium till it ceased to react, and had then used 20 drops* of decimal silver-solution, till this ceased to produce a further turbidity, we must now again add 20 drops of decimal solution of chloride of sodium, in order to reach the point at which this ceases to react. Were we to add only 10 instead of these 20 drops, we have the neutral point, as MULDER calls it, *i.e.*, the point at which both silver and chloride of sodium produce equal precipitates.

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* Twenty drops from Mulder's dropping apparatus are equal to 1 c. c.

We have, therefore, 3 different points to choose from for our final reaction: *a*, the point at which chloride of sodium has just ceased to precipitate the silver; *b*, the neutral point; *c*, the point at which silver solution has just ceased to precipitate chloride of sodium. Whichever we may choose, we must keep to it, *i.e.*, we must not use a different point in standardizing the chloride of sodium solution and in performing an analysis. The difference obtained by using first *a* and then *b* is, according to MULDER, for 1 grm. silver, at 16°, about 0·5 mgrm. silver; by employing first *a* and then *c*, as was permitted in the original process of GAY-LUSSAC, the difference is increased to 1 mgrm.

For our object, it appears most convenient to consider, once for all, the point *a* as the end, and never to finish with the silver-solution. If the point has been overstepped by the addition of too large an amount of decimal solution of chloride of sodium, 2 or 3 c. c. of decimal silver-solution should be added all at once. The end-point is then found by carefully adding decimal solution of chloride of sodium again, and the quantity of silver in the silver-solution added is reckoned from the original amount of silver weighed in making the solution.

c. PERFORMANCE OF THE PROCESS.

This is divided into two operations—*α*, the fixing of the value of the chloride of sodium solution; *β*, the assay of the silver alloy to be examined.

α. DETERMINATION OF THE VALUE OF THE CHLORIDE OF SODIUM SOLUTION, *i.e.*, its power of precipitating silver.

Weigh off exactly from 1·001 to 1·003 grm. chemically pure silver, put it into a test-bottle, add 5 c. c. perfectly pure nitric acid, of 1·2 sp. gr., and heat the bottle in an inclined position in a water- or sand-bath till complete solution is effected. Now blow out the nitrous fumes from the upper part of the bottle, and after it has cooled a little, place it in a stream of water, the temperature of which is about 16°, and let it remain there till its contents are cooled to this degree; wipe it dry, and place it in its case.

Now fill the 100 c. c. pipette with the concentrated solution of chloride of sodium, which is then allowed to flow into the test-bottle containing the silver solution.* Insert the glass stopper firmly (after moistening it with water), cover the neck of the bottle with the cap of black stuff belonging to it, and shake violently, without delay, till the chloride of silver settles, leaving the fluid perfectly clear. Then take the stopper out, rub it on the neck, so as to remove all chloride of silver, replace it firmly, and by giving the bottle a few dexterous turns, rinse the chloride down from the upper part. After allowing to rest a little, again remove the stopper, and add, from a burette divided into $\frac{1}{10}$ c. c., decimal chloride of sodium solution, allowing the drops to fall against the lower part of the neck, the bottle being held in an inclined position. If, as above directed, 1·001 to 1·003 grm. silver have been employed, the portions of chloride of sodium solution at first added may be ½ c. c. After each addition, raise the bottle a little out of its case, observe the amount of precipitate produced, shake till the fluid has become clear again, and proceed as above, before adding each fresh quantity of chloride of sodium solution. The smaller the precipitate produced, the smaller should be the quantity of chloride of sodium next added; towards the end only two drops should be added each time; and quite at the end read off the height of the fluid in the burette before each further addition. When the last two drops give no more precipitate, the previous reading is the correct one.

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* The pipette, having been filled above the mark, should be fixed in a support before the excess is allowed to run out, otherwise the measuring will not be sufficiently accurate.

If by chance the point has been overstepped, and the time has been missed for the proper reading off of the burette, add 2 to 3 c. c. of the decimal silver solution (the silver in which is to be added to the quantity first weighed), and try again to hit the point exactly by careful addition of decimal chloride of sodium solution.

The value of the chloride of sodium solution is now known. Reckon it to 1 grm. silver.

Suppose we had used for 1·002 grm. silver 100 c. c. of concentrated and 3 c. c. of decimal chloride of sodium solution; this makes altogether 100·3 of concentrated; then

$$1{\cdot}002 : 1{\cdot}000 :: 100{\cdot}3 : x$$
$$x = 100{\cdot}0998$$

We may without scruple put 100·1 for this number. We now know that 100·1 c. c. of the concentrated solution of chloride of sodium, measured at 16°, exactly precipitates 1 grm. of silver. This relationship serves as the foundation of the calculation in actual assaying, and must be re-examined whenever there is reason to imagine that the strength of the chloride of sodium solution may have altered.

β. THE ACTUAL ASSAY OF THE SILVER-ALLOY.

Weigh off so much as contains about 1 grm. of silver, or better, a few mgrm. more;* dissolve in a test-bottle in 5 to 7 c. c. nitric acid, and proceed in all respects exactly as in α.

Suppose we had taken 1·116 grm. of the alloy, and, in addition to the 100 c. c. of concentrated chloride of sodium solution, had used 5 c. c. of the dilute (= 0·5 concentrated), how much silver would the alloy contain?

Presuming that we use the same chloride of sodium solution which served as our example in α, 100·1 c. c. of which = 1 grm. silver, then

$$100{\cdot}1 : 100{\cdot}5 :: 1{\cdot}000 : x$$
$$x = 1{\cdot}003996 \text{ (say } 1{\cdot}004).$$

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* In coins, which consist of 9 parts of silver and 1 part of copper, therefore take about 1·115 or 1·120. In weighing off alloys of silver and copper, which do not correspond to the formula $Ag_3 Cu_4$ (standard $\doteq \frac{718{\cdot}71}{1000}$), we must remember that they are never homogeneous in the mass; thus, for instance, the pieces of metal from which coins are stamped, often show 1·5 to 1·7 in a thousand more silver in the middle than at the edges. In assaying alloys, then, portions from various parts of the mass must be taken, in order to get a correct result. The inaccuracy, however, proceeding from the cause above mentioned, can only be completely overcome by fusing the alloy, and taking out a portion from the well-stirred mass for the assay.

We may also arrive at the same result in the following manner:—

	Na Cl Solution.
For the precipitation of the silver in the alloy were used	100·5 c. c.
For 1 grm. silver are necessary	100·1 c. c.
Difference.....................	0·4 c. c.

There are, therefore, 4 mgrm. of silver present more than a grm., on the presumption that 0·1 of the concentrated chloride of sodium solution (=1 c. c. of the decimal solution) corresponds to 1 mgrm. silver. This supposition, although not absolutely correct, may be safely made, for the inexactness it involves is too minute, as is evident from the previous calculation.

Before we can execute this process exactly, we must know the quantity of silver the alloy contains very approximately. In assaying coins of known value this is the case, but with other silver alloys it is usually not so. Under the latter circumstances an approximate estimation must precede the regular assay. This is performed by weighing off ½ grm. (or in the case of alloys that are poor in silver, 1 grm.), dissolving in 3 to 6 c. c. nitric acid, and adding from the burette chloride of sodium solution, —first in larger, then in smaller quantities—till the last drops produce no further turbidity. The last drops are not reckoned with the rest. The operation is conducted, as regards shaking, &c., as previously given. Suppose we had weighed off 0·5 grm. of the alloy, and employed 25 c. c. of the chloride of sodium solution—taking the above supposed value of the latter—

We have $100{\cdot}1 : 25 : : 1{\cdot}000 : x$

$$x = 0{\cdot}2497$$

that is, the silver in ·5 grm. of the alloy; and as to the quantity of alloy we have to weigh off for the assay proper,

We have $\cdot 2497 : 1{\cdot}003 : : \cdot 5 : x$

$$x = 2{\cdot}008.$$

This quantity will, of course, require more nitric acid for solution than was previously used (use 10 c. c.). In cases where the highest degree of accuracy is not required, the results afforded by this rough preliminary estimation will be accurate enough if the experiment is carefully conducted, since they give the quantity of silver present to within $\frac{1}{1000}$ or $\frac{1}{500}$.

With alloys which contain sulphur, and with such as consist of gold and silver, and contain a little tin, LEVOL* employs concentrated sulphuric acid (about 25 grm.) as solvent. The portion of the alloy is boiled with it till dissolved; after cooling, the fluid is treated in the usual manner. As, however, concentrated sulphuric acid fails to dissolve all the silver when there is much copper present, MASCAZZINI † digests the weighed portion of alloy (which may contain small quantities of lead, tin, and antimony, besides gold) first with the least possible amount of nitric acid, as long as red vapors are formed; he then adds concentrated sulphuric acid, boils till the gold has settled well together, adds water after cooling, and then proceeds to the assay.

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* Annal. de Chim. et de Phys. 3 sér. 44, 347. † Chem. Centralbl. 1857, 800.

2. Pisani's Method.*

This process depends on the following reaction: a solution of iodide of starch added to a neutral solution of nitrate of silver forms iodide of silver and (in all probability) iodate of silver. The blue color consequently vanishes, and on continued additions of the iodide of starch, the fluid does not become permanently blue till all the nitrate of silver present is decomposed in the above manner. The iodide of starch solution used is therefore proportional to the quantity of nitrate of silver. Hence, if the value of the iodide of starch solution be determined, by allowing it to act on a certain amount of silver solution of known strength, we shall be able to estimate unknown quantities of silver with the greatest ease, provided that the silver solution is free from all other substances which exert a decomposing action on the iodide of starch. Besides the ordinary reducing agents, the following salts must be especially mentioned as possessing this power: the salts of suboxide and protoxide of mercury, of protoxide of tin, of teroxide of antimony, of arsenious acid, of protoxide of iron and of protoxide of manganese, also chloride of gold; salts of lead and of copper, on the other hand, do not affect iodide of starch.

The iodide of starch is prepared as follows: make an intimate mixture in a mortar of 2 grm. iodine and 15 grm. starch with the addition of 6 to 8 drops of water, and heat the slightly moist mixture in a closed flask in a water-bath, till the original violet-blue color has passed into dark grayish-blue—it takes about an hour. The iodide of starch thus prepared is then digested with water; it dissolves completely to a deep bluish-black fluid.

The value of this fluid is determined by allowing it to act on 10 c. c. of a neutral solution of nitrate of silver, containing 1 grm. of pure silver in 1 litre,—the silver solution is mixed with a little pure precipitated carbonate of lime before adding the iodide of starch. The strength of this latter is right, if 50 to 60 c. c. are used in this experiment. On adding it, at first the blue color disappears rapidly, and the fluid becomes yellowish from the iodide of silver. The end of the operation is attained as soon as the fluid is bluish-green. The point is pretty easy to hit, and an error of 0·5 c. c. is of no importance, as it only corresponds to about 0·0001 grm. of silver. The carbonate of lime, besides neutralizing the free acid, has the effect of rendering the final change of the color more distinctly observable. To analyze an alloy of silver and copper, dissolve about 0·5 grm. in nitric acid, dilute to 100 c. c. to lower the color of the copper, saturate 5 c. c. with carbonate of lime, and add iodide of starch till the coloration appears. Or, you may determine very approximately the amount of silver in 2 c. c. of the solution, then precipitate the greater part (about 99$\frac{0}{0}$) of the silver from 50 c. c. of the solution with standard solution of chloride of sodium, filter (for the chloride of silver also exercises a decolorizing action), and estimate the remainder of the silver by means of iodide of starch. If the amount of silver to be determined is more than 0·020 grm., it is always better to employ the latter method. In the case of a nitric acid solution containing silver with lead, the latter metal is first precipitated with sulphuric acid and filtered off, carbonate of lime is added to the filtrate till all free acid is neutralized, the fluid is filtered again (if necessary), and lastly, more carbonate of lime is added, and then the iodide of starch. Very dilute solutions may be concentrated, so that one may have no more than from 50 to 100 c. c. to deal with. The method is specially suited for the estimation of small quantities of silver. With such it has afforded me perfectly satisfactory results.

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* Annal. d. Min., x. 83.

Instead of the standard iodide of starch, a dilute standard solution of iodine in iodide of potassium may be equally well employed,—with addition of starch solution (FIELD [*]).

§ 116.

2. OXIDE OF LEAD.

a. Solution.

Few of the salts of lead are soluble in water. Metallic lead, oxide of lead, and most of the salts of lead that are insoluble in water dissolve in *dilute* nitric acid. Concentrated nitric acid effects neither complete decomposition nor complete solution, since, owing to the insolubility of nitrate of lead in concentrated nitric acid, the first portions of nitrate formed protect the yet undecomposed parts of the salt from the action of the acid. For the solubility of chloride and sulphate of lead, see § 83. As we shall see below, the analysis of these compounds may be effected without dissolving them. Iodide of lead dissolves readily in moderately dilute nitric acid upon application of heat, with separation of iodine. Solution of potassa is the only menstruum in which chromate of lead dissolves without decomposition; for the purpose of analysis, the chromate is best converted into the chloride (see below). Sulphide of lead may be converted at once into sulphate (see § 116, 2).

b. Determination.

Lead may be determined as *oxide*, *sulphate*, *chromate*, or *sulphide*; also by volumetric analysis.

We may convert into

1. OXIDE OF LEAD.

a. By Precipitation.

All salts of lead soluble in water, and those of its salts which, insoluble in that menstruum, dissolve in nitric acid, with separation of their acid.

b. By Ignition.

α. Salts of lead with readily volatile or decomposable inorganic acids.
β. Salts of lead with organic acids.

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[*] Chem. News, ii. 17.

2. SULPHIDE OF LEAD.

All salts of lead in solution.

3. SULPHATE OF LEAD.

a. By Precipitation.

The salts that are insoluble in water, but soluble in nitric acid, whose acid cannot be separated from the solution.

b. By Evaporation.

α. All the oxides of lead, and also the salts of lead with volatile acids.

β. Many of the organic compounds of lead.

4. CHROMATE OF LEAD.

The compounds of lead soluble in water or nitric acid.

The application of these several methods must not be understood to be rigorously confined to the compounds specially enumerated under their respective heads; thus, for instance, all the compounds enumerated sub 1, may likewise be determined as sulphate of lead; and, as above mentioned, all soluble compounds of lead may be converted into sulphide of lead; also, in sulphate of lead the lead may be without difficulty determined as sulphide. Chloride, bromide, and iodide of lead are most conveniently reduced to the metallic state in a current of hydrogen gas, in the manner described § 115 (Reduction of chloride of silver), if it is not deemed preferable to dissolve them in water, or to decompose them by a boiling solution of carbonate of soda. If the reduction method is resorted to, the heat applied should not be too intense, since this might cause some chloride of lead to volatilize.

The higher oxides of lead are reduced by ignition to the state of simple oxide, and may thus be readily analyzed and dissolved. Should the operator wish to avoid having recourse to ignition, the most simple mode of dissolving the higher oxides of lead is to act upon them with dilute nitric acid, with the addition of alcohol. For the methods of analyzing sulphate, chromate, iodide, and bromide of lead, I refer to the paragraphs treating of the corresponding acids, in the second part of this Section. To effect the estimation of lead in the oxide and in many salts of lead, especially also in the sulphate, the compound under examination may be fused with cyanide of potassium, and the metallic lead obtained well washed, and weighed. From the sulphide also the greater portion of the lead may be separated by this method, but never the whole (H. ROSE *).

1. *Determination as Oxide.*

a. By Precipitation.

Mix the moderately dilute solution with carbonate of ammonia † slightly in excess, add some caustic ammonia, apply a gentle heat, and, after some time, filter. Wash the precipitate with pure water, dry, and ignite in a porcelain crucible, having previously incinerated the filter on the lid. For the properties of the precipitate and residue, see § 83. The results are satisfactory, although generally a trifle too low, owing to carbonate of lead not being absolutely insoluble, particularly in fluids rich in ammoniacal salts (Expt. No. 47). A small and thin filter should be used, and care taken to remove the precipitate as completely as practicable before proceeding to incineration; otherwise additional loss of substance might be incurred, from reduction of the adhering particles of the carbonate to metallic lead.

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* Pogg. Annal. 91, 144.

† Oxalate of ammonia, which has been so highly recommended as a precipitant for lead, is not so delicate as the carbonate. My experience in this respect coincides with F. Mohr's (Expt. No. 48).

b. By Ignition.

Compounds like carbonate or nitrate of lead are cautiously ignited in a porcelain crucible, until the weight remains constant. In case of salts of lead with organic acids, the substance is very gently heated in a small covered porcelain crucible, which is included within a large one, also covered, until the organic matter is completely carbonized; the lids are then removed, when the mass begins to ignite, and a mixture of oxide of lead with metallic lead results, which may still contain unconsumed carbon. A few pieces of recently fused nitrate of ammonia are now thrown into the inner crucible, which has previously been removed from the flame, and both are again covered. The salt fuses, oxidizes the lead, and converts it partly into nitrate. The whole is now very gradually raised to a red heat, until no more fumes of hyponitric acid escape. The residuary oxide is then weighed.

The results are satisfactory.

2. *Determination as Sulphide.*

Lead may be completely precipitated from acid, neutral, and alkaline solutions by sulphuretted hydrogen, and also from neutral and alkaline solutions by sulphide of ammonium. Precipitation from acid solution is usually employed, especially in separations. A large excess of acid and also warming should both be avoided. The former is prejudicial to complete precipitation (§ 83, e), the latter may readily occasion the re-solution of the sulphide that has already been precipitated. In order to guard against incomplete precipitation, before filtering, test a portion of the supernatant fluid by mixing with a relatively large quantity of strong sulphuretted hydrogen water; of course the mixture should remain clear.

After the sulphide has been filtered off, washed with cold water, and dried, it is transferred, together with the filter-ash, to a porcelain crucible, a little sulphur added, and ignited in hydrogen till its weight is constant. It should always be allowed to cool in a current of the gas, before being weighed. As regards the apparatus, see § 108, 2, fig. 47. For the properties of the residue, see § 83, e. The results are very satisfactory (H. Rose). The heat of the ignition must not be too low, or the residue will contain too much sulphur; nor too high, or the sulphide of lead will begin to volatilize.* Drying the precipitate at 100°

[* According to SOUCHAY, the ignition must not last more than 5–10 minutes, and only the base of the crucible (to one-fourth its height) should be heated to redness; even then the result is likely to fall out slightly too low. Fres. Zeitschrift, IV. 65.]

cannot be recommended (§ 83, e). If, for want of a suitable apparatus, the ignition in hydrogen cannot be performed, the dry sulphide may be converted into sulphate and then weighed. To this end it is transferred to a beaker, the filter-ash added, then fuming nitric acid, drop by drop, the vessel being kept covered with a glass plate. When the oxidation is finished, a gentle heat is applied for some time, and the contents of the beaker are then poured into a small porcelain dish, the former is rinsed, a few drops of sulphuric acid are added, the mixture is carefully evaporated, and the residue ignited. The accuracy of the result is entirely dependent on the care with which the operation is conducted. Fuming nitric must be used, as directed, for oxidizing the precipitate, otherwise sulphur separates, which, on warming with weaker acid, fuses, and only oxidizes with extreme slowness.

3. *Determination as Sulphate.*

a. By Precipitation.

α. Mix the solution (which should not be over-dilute) with moderately dilute pure sulphuric acid slightly in excess, and add to the mixture double its volume of spirit of wine; wait a few hours, to allow the precipitate to subside; filter, wash the precipitates with spirit of wine, dry, and ignite, after the method described in § 53. Though a careful operator may use a platinum crucible, still a thin porcelain crucible is preferable. A small and thin filter should be employed, and the adhering sulphate of lead carefully removed before proceeding to incineration (see 1, *a*).

β. In cases where the addition of spirit of wine is inadmissible, a greater excess of sulphuric acid must be used, and the precipitate, which is allowed some time to subside, filtered, and washed first with water acidulated with a few drops of sulphuric acid, then repeatedly with spirit of wine. The remainder of the process is conducted as in *α*.

For the properties of the precipitate, see § 83. The method *α* gives accurate results; those obtained by *β* are less exact (a little too low), but still, however, satisfactory, if the directions given are adhered to. If, on the contrary, a proper excess of sulphuric acid is not added, in the presence, for instance, of ammoniacal salts, nitric acid, &c., the lead is not completely precipitated, and if pure water is used for washing, decided traces of the precipitate are dissolved.

b. By Evaporation.

α. Put the substance into a weighed dish, dissolve in dilute nitric acid, add moderately dilute pure sulphuric acid slightly in excess, and evaporate at a gentle heat, best over a heated iron cup, until the excess of sulphuric acid is completely expelled. In the absence of organic substances, the evaporation may be effected without fear in a platinum dish; but if organic substances are present, a light porcelain dish is preferable. With due care in the process of evaporation, the results are perfectly accurate.

β. Organic compounds of lead are converted into the sulphate by treating them, in a porcelain crucible, with pure concentrated sulphuric acid in excess, evaporating cautiously in the well-covered crucible until the excess of sulphuric acid is completely expelled, and igniting the residue. Should the latter not look perfectly white, it must be moistened once more with sulphuric acid, and the operation repeated. The method gives, when conducted with great care, accurate results; a trifling loss is, however, usually incurred, the escaping sulphurous acid and carbonic acid gases being liable to carry away traces of the salt.

4. *Determination as Chromate of Lead.*

If the solution is not already distinctly acid, render it so with acetic acid, then add bichromate of potassa in excess, and, if free nitric acid has been present, add acetate of soda in sufficient quantity to replace the free nitric acid by free acetic acid; let the precipitate subside at a gentle heat, and collect on a weighed filter dried at 100°; wash with water, dry at 100°, and weigh. The precipitate may also be ignited according to § 53, but in this case care must be taken that hardly any of the salt remains adhering to the paper, and that the heat is not too high. For the properties of the precipitate, see § 93, 2. The results are accurate. (Expt. No. 76.)

5. *Determination of Lead by Volumetric Analysis.*

H. Schwarz's new method.* To the nitric acid solution add ammonia or carbonate of soda, as long as the precipitate redissolves on shaking; mix with acetate of soda in not too small quantity, and then run in from a burette a solution of bichromate of potash (containing 14·759 grm. in the litre) till the precipitate begins to settle rapidly. Now place on a porcelain plate a number of drops of a solution of neutral nitrate of silver, and proceed with the addition of the chromate, two or three drops at a time, stirring carefully after each addition. When the precipitate has settled tolerably clear, which takes only a few seconds, remove a drop of the supernatant liquid and mix it with one of the drops of silver on the plate. A small excess of chromate gives at once a distinct red coloration; the precipitated chromate of lead does not act on the silver solution, but remains suspended in the drop. The number of c. c. of solution of chromate used (*minus* 0·1, which Schwarz deducts for the excess) multiplied by 0·0207 = the quantity of lead. If the fluid appear yellow before the reaction with the silver salt occurs, acetate of soda is wanting. In such a case, first add more acetate of soda, then 1 c. c. of a solution containing 0·0207 lead in 1 c. c., complete the process in the usual way, and deduct 1 c. c. from the quantity of chromate used on account of the extra lead added. Any iron present must be in the form of sesquioxide; metals whose chromates are insoluble, must be removed before the method can be employed.

§ 117.

3. Suboxide of Mercury.

a. Solution.

Suboxide of mercury and its compounds may generally be dissolved by means of dilute nitric acid, but without application of heat if conversion of any of the suboxide into oxide is to be avoided. If all that is required is to dissolve the mercury, the easiest way is to warm the substance for some time with nitric acid, then add hydrochloric acid, drop by drop, and continue the application of a moderate heat until a perfectly clear solution is produced, which now contains all the mercury as oxide and chloride. Heating the solution to boiling must be carefully avoided, as otherwise chloride of mercury may escape with the steam.

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* Dingl. Polyt. Journ. 169, 284.

b. Determination.

If it is impracticable to produce a solution of the suboxide or its compounds perfectly free from oxide, and it becomes accordingly necessary to convert the mercury completely into oxide, the latter is determined as directed § 118. But if a solution of suboxide has been obtained, quite free from oxide, the determination of the suboxide may be based upon the insolubility of subchloride of mercury, and effected either gravimetrically or volumetrically. The process of determining mercury, described § 118, 1, *a*, may, of course, be applied equally well in the case of compounds of suboxide of mercury.

1. *Determination as Subchloride of Mercury.*

Mix the cold highly dilute solution with solution of chloride of sodium, as long as a precipitate forms; let the precipitate subside, collect on a weighed filter, dry at 100°, and weigh. For the properties of the precipitate, see § 84. Results accurate.

If the solution of suboxide of mercury contains much free nitric acid, the greater part of this should be neutralized with carbonate of soda before adding the chloride of sodium.

2. *Volumetric Methods.*

Several methods have been proposed under this head: the following are those which are most worthy of recommendation:—

a. Mix the cold solution with decinormal solution of chloride of sodium (§ 117, $^{\beta}$), until this no longer produces a precipitate, and is accordingly present in excess; filter and wash thoroughly, taking care, however, to limit the quantity of water used; add a few drops of solution of chromate of potassa, then pure carbonate of soda, sufficient to impart a light yellow tint to the fluid, and determine, by means of solution of nitrate of silver (§ 141, *b*, *α*), the quantity of chloride of sodium in solution, consequently the quantity which has been added in excess; this shows, of course, also the amount of chloride of sodium consumed in effecting the precipitation. One equivalent of Hg_2O is reckoned for every equivalent of Na Cl, consequently for every c. c. of the decinormal solution of chloride of sodium, 0·0208 grm. of suboxide of mercury. As filtering and washing form indispensable parts of the process, this method affords no great advantage over the gravimetric; however, the results are accurate (FR. MOHR[*]). The two methods, 1 and 2, *a*, may also be advantageously combined.

b. The solution containing the mercury in the form of suboxide is diluted with enough water, gently warmed, and solution of hyposulphite of soda—12·4 grms. in the litre—added (waiting a little and shaking vigorously after each addition), till the last drop gives no brown coloration. The subsulphide of mercury formed subsides well and quickly, and the end of the reaction is easy to perceive ($Hg_2O, NO_5 + NaO, S_2O_2 = Hg_2S + NaO, SO_3 + NO_5$). Each 1 c. c. of the solution employed =·0208 suboxide of mercury or ·0200 mercury. Results accurate (J. J. SCHERER[†]).

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[*] Lehrbuch der Titrirmethode, ii. 62. [†] His Lehrbuch der Chemie, 1, 511.

§ 118.

4. OXIDE OF MERCURY.

a. Solution.

Oxide of mercury, and those of its compounds which are insoluble in water, are dissolved, according to circumstances, in hydrochloric acid or in nitric acid. Sulphide of mercury is heated with hydrochloric acid, and nitric acid or chlorate of potassa added until complete solution ensues; it is, however, most readily dissolved by suspending it in dilute potassa and transmitting chlorine, at the same time gently warming (H. ROSE). When a solution of chloride of mercury is evaporated on the water-bath, chloride of mercury escapes with the aqueous vapor.

b. Determination.

Mercury may be weighed in the *metallic state*, or as *subchloride*, *sulphide*, or *oxide* (84); in separations it is sometimes determined as loss on ignition. It may also be estimated volumetrically.

The three first methods may be used in almost all cases; the determination as oxide, on the contrary, is possible only in compounds of the oxide or suboxide with nitric acid. The methods by which the mercury is determined as subchloride or sulphide are to be preferred before those in which it is separated in the metallic form. Of the volumetric methods the first can be employed in many cases, while the second and third are only of very limited application.

1. *Determination as Metallic Mercury.*

a. In the Dry Way.

The process is conducted in the apparatus illustrated by fig. 50.

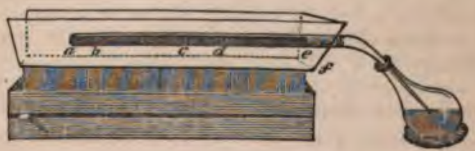

Fig. 50.

Take a tube eighteen inches long, and about four lines wide, made of difficultly fusible glass, and sealed at one end. First put into the tube a mixture of bicarbonate of soda and powdered chalk, then a layer of quick-lime; these two will occupy the space from *a* to *b*. (Let the mixture for generating carbonic acid take up about two inches). Then add the intimate mixture of the substance with an excess of quick-lime (*b–c*), then the lime-rinsings of the mortar (*c–d*), then a layer of quick-lime (*d–e*), and lastly, a loose stopper of asbestus (*e–f*). The anterior end of the tube is then drawn out, and bent at a somewhat obtuse angle. The manipulations in the processes of mixing and filling being the same as in organic analysis, they will be found in detail in the chapter on that subject.

A few gentle taps upon the table are sufficient to shake the contents of the tube down so as to leave a free passage through the whole length of the tube. The tube, so prepared and arranged, is now placed in a combustion furnace, the point being inserted into a flask containing water, the surface of which it should just touch, so that the opening may be just closed.

The tube is now surrounded with red-hot charcoal, in the same way as in organic analysis, proceeding slowly from *e* to *a*, the last traces of mercurial vapor being expelled by heating the mixture at the sealed end of the tube. Whilst the tube still remains in a state of intense ignition, the neck is cut off at *f*, and carefully and completely rinsed into the receiving flask, by means of a washing-bottle. The small globules of mercury which have distilled over are united into a large one, by agitating the flask, and, after the lapse of some time, the perfectly clear water is decanted, and the mercury poured into a weighed porcelain crucible, where the greater portion of the water still adhering to it is removed with blotting-paper. The mercury is then finally dried under a bell-jar, over concentrated sulphuric acid, until the weight remains constant. Heat must not be applied. For the properties of the metal, see § 84. In the case of sulphides, in order to avoid the presence of vapor water in the tube, which would give rise, to the formation of sulphuretted hydrogen, the mixture of bicarbonate of soda and chalk is replaced by magnesite. Iodide of mercury cannot be completely decomposed by lime. To analyze this in the dry way, substitute finely divided metallic copper for the lime (H. Rose [*]). The accuracy of the results is entirely dependent upon the care bestowed. The most highly accurate results are, however, obtained by the application of the somewhat more complicated modification adopted by Erdmann and Marchand for the determination of the atomic weight of mercury and of sulphur. For the details of this modified process, I refer to the original essay,[†] simply remarking here, that the distillation is conducted, in a combustion-tube, in a current of carbonic gas, and that the distillate is received in a weighed bulb apparatus with the outer end filled with gold-leaf, to insure the condensation of every trace of mercury vapor. This way of receiving and condensing may be employed also in the analysis of amalgams (König [‡]).

b. In the Wet Way.

The solution, free from nitric acid, and mixed with free hydrochloric acid, is precipitated, in a flask, with an excess of a clear solution of protochloride of tin, containing free hydrochloric acid; the mixture is boiled for a short time, and then allowed to cool. After some time, the perfectly clear supernatant fluid is decanted from the metallic mercury, which, under favorable circumstances, will be found united into one globule; if this is the case, the globule of mercury may be washed at once by decantation, first with water acidulated with hydrochloric acid, and finally with pure water; it is dried as in *a*.

If, on the other hand, the particles of the mercury have not united, their union in one globule may as a rule be readily effected by boiling a short time with some moderately dilute hydrochloric acid mixed with a

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[*] Pogg. Annal. 110, 546.

[†] Journ. f. prakt Chem. 31, 385; also Pharm. Centralbl. 1844, 354.

[‡] Journ. f. prakt. Chem. 70, 64.

[illegible] removed by [illegible] of metallic [illegible]

[illegible] may be used [illegible] This method [illegible] the greatest care. In [illegible]

[illegible]

[illegible] which may contain [illegible] and [illegible]

[illegible] which may [illegible]

[illegible]

[illegible] repeated, [illegible] on the [illegible]

[illegible] very large, it may [illegible] is first washed with water, then [illegible] with bisulphide of carbon, till a few drops of the washings evaporate on a watch-

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* Pogg. Annal. 110, 529

† Annal. d. Chem. u. Pharm. 107, 97 ; and 110, 177.

‡ Journ. f. prakt. Chem. 77, 73.

glass without leaving a residue. (The precipitate is retained on the filter throughout this operation.)

Properties of the sulphide of mercury, § 84.

4. *Determination as Oxide.*

In the salts of the oxides of mercury, with nitrogen acids, the metal may be very conveniently determined in the form of oxide (MARIGNAC [*]). For this purpose, the salt is heated in a bulb-tube, of which the one end, drawn out to a point, dips under water, the other end being connected with a gasometer, by means of which dry air is transmitted through the tube, as long as the application of heat is continued. In this way complete decomposition of the salt is readily effected, without reaching the temperature at which the oxide itself would be decomposed.

5. *Volumetric Methods.*

After J. J. SCHERER.[†] The nitrate or chloride of mercury may be directly determined with hyposulphite of soda. The reactions are as follows: $3\,(Hg\,O, N\,O_5) + 2\,(Na\,O, S_2\,O_2) = (2\,Hg\,S + Hg\,O, N\,O_5) + 2\,(Na\,O, S\,O_3) + 2\,N\,O_5$ and $3\,Hg\,Cl + 2\,(Na\,O, S_2\,O_2) + 2\,H\,O = (2\,Hg\,S, Hg\,Cl) + 2\,(Na\,O, SO_3) + 2\,H\,Cl$. The process is conducted as follows in the case of nitrate of mercury: Mix the highly dilute solution with a little free nitric acid in a tall glass and add drop by drop solution of hyposulphite of soda—12·4 grm. in a litre. Each drop produces an intense yellow cloud, which on shaking quickly subsides in the form of a heavy flocculent precipitate $(2\,Hg\,S + Hg\,O, N\,O_5)$. In order to distinguish clearly the exact end of the reaction, SCHERER recommends to transfer the fluid towards the end to a measuring flask, to take out $\frac{1}{3}$ or $\frac{1}{2}$ of the clear fluid and to finish with this. The portion of hyposulphite last used is multiplied by 3 or 2, as the case may be, and added to the quantity first used. 1 c. c. of the solution corresponds to ·015 mercury, or ·0162 oxide of mercury. The relation is not changed even when the fluid contains another acid (sulphuric, phosphoric).

In the case of chloride of mercury, the highly dilute solution is mixed with a little hydrochloric acid and warmed, nearly to boiling, before beginning to add the hyposulphite of soda. At first a white turbidity is formed, then the precipitate separates in thick flocks. When the solution begins to appear transparent, the precipitant is added more slowly. In order to hit the end of the reaction exactly, small portions must be filtered off towards the close. The precipitate must be completely white; if too much hyposulphite has been added, it is gray or blackish, and the experiment must be repeated. SCHERER obtained very accurate results. Of course no other metals must be present that exert a decomposing action on hyposulphite of soda.

§ 119.

5. OXIDE OF COPPER.

a. Solution.

Metallic copper is best dissolved in nitric acid. Oxide of copper, and those of its salts which are insoluble in water, may be dissolved in nitric, hydrochloric, or sulphuric acid. Sulphide of copper is treated with fuming nitric acid, or it is heated with moderately dilute nitric acid, until the separated sulphur exhibits a pure yellow tint; addition of a little hydrochloric acid or chlorate of potassa greatly promotes the action of the dilute acid. [Native sulphides are easily decomposed by a mixture of strong nitric and sulphuric acids.]

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[*] Jahresber. von Liebig u. Kopp, 1849, 594.

[†] His Lehrbuch der Chemie, i. 513.

b. Determination.

Copper may be weighed in the form of *oxide*, or in the *metallic state*, or as *subsulphide* (§ 85). Into the form of oxide it is converted by precipitation or ignition, sometimes with previous precipitation as sulphide. The determination as subsulphide is preceded usually by precipitation either as sulphide or as sulphocyanide. Copper may be determined also by various volumetric and indirect methods.

We may convert into

1. Oxide of Copper.

a. By direct Precipitation as Oxide.

All salts of oxide of copper soluble in water, and also those of the insoluble salts, the acids of which may be removed upon solution in nitric acid, provided no non-volatile organic substances be present.

b. By Precipitation, preceded by Ignition of the Compound.

Such of the salts enumerated sub *a* as contain a non-volatile organic substance, thus more particularly salts of copper with non-volatile organic acids.

c. By Precipitation as Sulphide of Copper.

All compounds of copper without exception.

d. By Ignition.

Salts of copper with oxygen acids that are readily volatile or decomposable at a high temperature (carbonate of copper, nitrate of copper).

2. Metallic Copper.

Oxide of copper in all solutions free from other metals precipitable by zinc.

3. Subsulphide of Copper.

Oxide of copper in all cases in which no other metals are present that are precipitable by sulphuretted hydrogen, hyposulphite of soda, or sulphocyanide of potassium.

Of the methods of estimating copper, I prefer—in all cases where the choice is left free and where precipitation cannot be avoided—method 2, as the process is more rapidly performed than is the case with method 1, while the results are, at least, equally accurate. Method 3 finds application chiefly in separations of copper from other metals, and is, as now carried out, very exact and convenient. The volumetric methods are especially adapted for technical purposes, but they are inferior to method 2 in simplicity and accuracy.

1. *Determination as Oxide of Copper.*

a. By direct Precipitation as Oxide.

α. From Neutral or Acid Solutions.

Heat the *rather dilute* solution in a platinum or porcelain dish, to incipient ebullition, add a somewhat dilute solution of pure soda or potassa until the formation of a precipitate ceases, and keep the mixture a few minutes longer at a temperature near boiling. Allow to subside, filter off the fluid, wash the precipitate by decantation twice or thrice, boiling up each time, then collect it on the filter, wash thoroughly with hot water, dry, and ignite in a platinum crucible, as directed § 53. After intense ignition, and having added the ash of the filter, let the crucible cool in the desiccator, and weigh. The action of reducing gases must be carefully guarded against in the process of ignition.

It will sometimes happen, though mostly from want of proper attention to the directions here given, that particles of the oxide of copper adhere so tenaciously to the dish as to be mechanically irremovable. In a case of this kind, after washing the dish thoroughly, dissolve the adhering particles with a few drops of nitric acid, and evaporate the solution over the principal mass of the precipitated oxide, before you proceed to ignite the latter. Should the solution be rather copious, it must first be concentrated by evaporation, until only *very little* of it is left. For the properties of the precipitate, see § 85.

With proper attention to the directions here given, the results obtained by this method are quite accurate, otherwise they may be either too high or too low. Thus, if the solution be not sufficiently dilute, the precipitant will fail to throw down the whole of the oxide of copper; or, if the precipitate be not thoroughly washed with hot water, it will retain a portion of the alkali; or, if the ignited precipitate be allowed to stand exposed to the air, before it is weighed, an increase of weight will be the result; and so, on the other hand, a diminution of weight, if the oxide be ignited with the filter or under the influence of reducing gases, as thereby suboxide would be formed. Should a portion of the oxide have suffered reduction, it must be reoxidized by moistening with nitric acid, evaporating cautiously to dryness, and exposing the residue to a gentle heat, increasing this gradually to a high degree of intensity.

Let it be an invariable rule to test the filtrate for copper with sulphuretted hydrogen water. If, notwithstanding the strictest compliance with the directions here given, the addition of this reagent produces a precipitate, or imparts a brown tint to the fluid, this is to be attributed to the presence of organic matter; in that case, concentrate the filtrate and wash-water by evaporation, acidify, precipitate with sulphuretted hydrogen water, treat the precipitated sulphide as directed in *c*, and add the oxide obtained to the first precipitate in the filter. It is also highly advisable not to neglect dissolving the oxide of copper, after weighing, in hydrochloric acid, in order to detect, and, if necessary, estimate, any silicic acid which might be present.

β. *From Alkaline Solutions.*

From ammoniacal solutions also, oxide of copper may be precipitated by soda or potassa. In the main, the process is conducted as in α. After precipitation the mixture is heated, until the supernatant fluid has become perfectly colorless; the fluid is then filtered off with the greatest possible expedition. If allowed to cool with the precipitate in it a small portion of the latter would redissolve.

b. By Precipitation as Oxide, preceded by Ignition of the Substance.

Heat the substance in a porcelain crucible, until the organic matter [illegible] the residue in dil[illegible] acid, [illegible] solution as directed [illegible].

[illegible] Copper.

[illegible] st neutral, or slightly [illegible], but [illegible] nitric acid—according to the quan- [illegible] addition of strong sulphuretted hy- [illegible]. When the precipitate has fully [illegible] that the supernatant fluid is no longer [illegible] *sulphuretted hydrogen water*, filter off [illegible] at intermission with water contain- [illegible] prevent oxidation),* and dry on the filter [illegible] the dried precipitate to a beaker, incine- [illegible] ain dish, add the ash to the precipitate, [illegible] nitric acid, add some hydrochloric acid, and [illegible] sulphur appears of a pure yellow color; [illegible], and precipitate as directed in *a*.

[illegible] the copper, as sulphide, with hydrosul- [illegible] sulphide, it may also be precipitated with [illegible] this end, the solution of copper (which, if ne- [illegible] far as practicable from hydrochloric acid and [illegible] with sulphuric acid) is sufficiently diluted, [illegible] with a solution of hyposulphite of soda, as [illegible] forms. As soon as this has subsided, leaving [illegible] in the supernatant fluid, the precipitation of [illegible] The precipitate is subsulphide of copper (Cu_2 [illegible] washed without risk of oxidation (FLAJOLOT†). [illegible] to oxide as directed in 1, *a*.

[illegible] the sulphide or subsulphide of copper into ox- [illegible] weigh them as subsulphide, see 3.

[illegible] a platinum or porcelain crucible, and exposed to [illegible] is gradually increased to intense redness; the [illegible].

[illegible] spirts strongly when ignited, it is always advisa- [illegible] small covered platinum crucible, and to place the [illegible] also covered. With proper care, the results are [illegible] salts with organic acids may also be converted into [illegible] tion. To this end, the residue first obtained, which [illegible] completely oxidized, by repeated moistening with [illegible] ation. However, a loss of substance is generally in- [illegible], from the difficulty of avoiding spirting.

[illegible] as Metallic Copper.‡

[illegible] tion with Zinc.

[illegible] the solution of copper, after having, if required, first freed

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[*] Mohr finds that sulphide of copper, when precipitated at a boiling heat by HS from solution of the sulphate, does not oxidize by exposure to the air, and washes easily.

[†] Journ. f. prakt. Chem. 61, 105.

[‡] The method of precipitating copper by iron or zinc, and weighing it in the metallic form, was proposed long ago; see Pfaff's Handbuch der analytischen Chemie. Altona, 1822, Bd. 2, Seite 269, where the reasons are given for prefer-

it from nitric acid, by evaporation with hydrochloric acid or sulphuric acid, into a weighed platinum dish; dilute, if necessary, with some water, throw in a piece of zinc, soluble in hydrochloric acid without residue, and add, if necessary, hydrochloric acid in sufficient quantity to produce a moderate evolution of hydrogen. If, on the other hand, this evolution should be too brisk, owing to too large excess of acid, add a little water. Cover the dish with a watch-glass, which is afterwards rinsed into the dish with the aid of a washing-bottle. The separation of the copper begins immediately; a large proportion of it is deposited on the platinum in form of a solid coating; another portion separates, more particularly from concentrated solutions, in the form of red spongy masses. Application of heat, though it promotes the reaction, is not absolutely necessary; but there must always be sufficient free acid present to keep up the evolution of hydrogen. After the lapse of about an hour or two, the whole of the copper has separated. To make sure of this, test a small portion of the supernatant fluid with sulphuretted hydrogen water; if this fails to impart a brown tint to it, you may safely assume that the precipitation of the copper is complete. Ascertain now, also, whether the zinc is entirely dissolved, by feeling about for any hard lumps with a glass rod, and observing whether renewed evolution of hydrogen will take place upon addition of hydrochloric acid. If the results are satisfactory in this respect also, press the copper together with a glass rod, decant the clear fluid, which is an easy operation, pour, without loss of time, boiling water into the dish, decant again, and repeat this operation until the washings are *quite* free from hydrochloric acid. Decant the water now as far as practicable, rinse the dish with strong alcohol, place in the water-bath, and, when the copper is perfectly dry, let it cool, and weigh. If you have no platinum dish, the precipitation may be effected also in a porcelain crucible or glass dish; but it will, in that case, take a longer time, owing to the absence of the galvanic antagonism between platinum and zinc; and the whole of the copper will be obtained in loose masses, and not firmly adhering to the sides of the crucible or dish, as in the case of precipitation in platinum vessels.

The results are very accurate. The direct experiment, No. 78, gave 100·0 and 100·06, instead of 100. FR. MOHR (*loc. cit.*) obtained equally satisfactory results by precipitating in a porcelain crucible.*

b. By Precipitation with a Hypophosphite.

The rather concentrated solution in sulphuric acid (chlorine and nitric acid must not be present) is treated with excess of a solution of a hypophosphite in the cold, and then gradually warmed on the water-bath to 80°–90°. The copper shortly separates in coherent masses of hydride of copper. When the precipitation is complete, as may be ascertained by means of sulphuretted hydrogen, or other appropriate test, the precipitate is washed with hot water by decantation, transferred to a porcelain crucible, as described on p. 207, and, after drying, ignited and cooled in a stream of hydrogen gas (fig. 47, p. 181), or it is collected on a filter,

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ring zinc as a precipitant, and sulphuretted hydrogen is recommended as a test for ascertaining whether the precipitation is complete. I mention this with reference to Fr. Mohr's paper in the Annal. d. Chem. u. Pharm. 96, 215, and Bodemann's Probirkunst von Kerl, Seite 220.

* Storer (On the alloys of copper and zinc, Cambridge, 1860, p. 47) says that the precipitated copper retains water, but I have not found this to be the case (See Expt. No. 79).

and, after calcination, weighed in a close crucible as oxide. Results very accurate (GIBBS [*]).

3. *Determination as Subsulphide of Copper.*

a. By Precipitation as Sulphide.—Precipitate the copper as in 1, *c*, dry, transfer to a porcelain crucible, add the filter-ash and some pure powdered sulphur and ignite strongly in a stream of hydrogen (§ 108, fig. 47). It is advisable to use a gas blast-lamp. The results are very accurate (H. ROSE [†]).

b. By Precipitation as Subsulphocyanide, after RIVOT. [‡]—The solution should be as free as possible from nitric acid and free chlorine, and not too acid. Add sulphurous or hypophosphorous acid in sufficient quantity, and then solution of sulphocyanide of potassium. The copper precipitates as white subsulphocyanide. It is filtered after standing some time, washed and dried, mixed with sulphur, ignited in hydrogen in the apparatus alluded to in *a*, and this ignition with sulphur is repeated till the weight is constant. The precipitate may also be collected on a weighed filter, dried at 100°, and then weighed. The experiment, No. 80, conducted in the latter way, gave 99·66 instead of 100.

c. Oxide and suboxide of copper, sulphate, and many other salts of copper may be directly converted into subsulphide, by mixing with sulphur and igniting in hydrogen as in *a* (H. ROSE, *loc. cit.*). The results are thoroughly satisfactory.

4. *Volumetric Methods.*

Of the numerous proposals under this head, the following are the best.

a. DE HAEN'S Method.[§]

I recommend this method, which was devised in my own laboratory,[‖] as more especially applicable in cases where small quantities of copper are to be estimated in an expeditious way. The method is based upon the fact that, when a salt of oxide of copper in solution is mixed with iodide of potassium in excess, subiodide of copper and free iodine are formed, the latter remaining dissolved in the solution of iodide of potassium: $2(CuO, S O_3) + 2 K I = Cu_2 I + 2 (K O, S O_3) + I$. Now, by estimating the iodine by BUNSEN'S method, or with hyposulphite of soda (§ 146), we learn the quantity of copper, as 1 eq. iodine (127) corresponds to 2 eq. copper (63·4). The following is the most convenient way of proceeding. Dissolve the compound of copper in sulphuric acid, best to a neutral solution; a moderate excess of free sulphuric acid, however, does not injuriously affect the process. Dilute the solution, in a measuring flask, to a definite volume; 100 c. c. should contain from 1 to 2 grms. oxide of copper. Introduce now about 10 c. c. of iodide of potassium solution (1 iodide of potassium in 10 water) into a large beaker, add 10 c. c. of the copper solution, mix, and then proceed *without delay* to determine the separated iodine by means of hyposulphite of soda (§ 146). It is scarcely necessary to mention that the copper solution must be free from sesquioxide of iron and other bodies which decompose iodide of potassium, also free nitric acid, and free hydrochloric acid. With strict attention to these rules, the results are accurate. De Haen obtained, for instance, 0·3567 instead of 0·3566 of sulphate of copper, 99·89 and 100·1 instead of 100 of metallic copper. Further experiments (No. 81) have convinced me, however, that, though the results attainable by this method are satisfactory, they are not always quite so accurate as would be supposed from the above figures given by De Haen. Acting upon Fr. Mohr's suggestion, I tried to counteract the injurious influence of the presence of nitric acid, by adding to the solution containing nitric acid first ammonia in excess, then hydrochloric acid to slight excess; the result was by no means satisfactory. The reason of this is that a solution of nitrate of ammonia, mixed with some hydrochloric acid, will, even after a short time, begin to liberate iodine from solution of iodide of potassium.

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[*] Am. Journ. Sci. 2d Ser. xliv. 210.

[†] Compt. rend. 38, 868; Journ. f. prakt. Chem. 62, 252.

[‡] Pogg. Annal. 110, 138.

[§] Annal. d. Chem. u. Pharm. 91, 237.

[‖] Brown (Quart. Journ. of the Chem Soc. x. 65), who published this as a new method in 1857, must have been ignorant of its previous publication in 1854. The little variation, too, of determining the iodine with hyposulphite of soda (according to Schwarz) instead of with sulphurous acid (according to Bunsen), may be found in Mohr's Lehrbuch der Titrirmethode, i. 387 (1855).

b. Carl Mohr's Method; H. Fleck's Modification.[*]

The proposal to take the action of solution of cyanide of potassium on ammoniacal solution of copper as the foundation of a method for estimating copper is due to Carl Mohr.[†]

The azure-blue color disappears, $Cu_2\,Cy$, $N\,H_4\,Cy$ and $K\,O$ are formed, while 1 eq. cyanogen is separated, which, acting on the free ammonia, gives urea, oxalate of urea, cyanide of ammonium and formiate of ammonia (Liebig [‡]).

The decomposition is not always the same, the quantity and degree of concentration of the ammonia has a marked influence on it, comp. Liebig (*loc. cit.*), also my own experiments (No. 82, *a*), from which it appears that neutral ammonia salts also affect the results.

Fleck (*loc. cit.*) proposes the following modification:—

Instead of caustic ammonia use a solution of sesquicarbonate of ammonia (1 in 10), warm the mixture to about 60°, and in order to render the end-reaction plainer add 2 drops of solution of ferrocyanide of potassium (1 in 20); the blue color of the solution is not altered by this addition, nor is its clearness affected. The value of the cyanide of potassium solution is first determined, by means of copper solution of known strength, and it is then employed on the copper solution to be examined. On dropping the cyanide of potassium into the blue solution warmed to 60°, the odor of cyanogen is plainly perceptible, and the color gradually disappears. As soon as the ammoniacal double salt of copper is destroyed, the solution becomes red from the formation of ferrocyanide of copper, without any precipitate appearing, and with the addition of a final drop of cyanide of potassium this red color in its turn vanishes, so that the fluid now appears quite colorless.

The method thus modified yields, it is true, better, but still only approximate, results.[§] Where such are good enough, the method is certainly convenient. I have found that the presence of ammonia salts is here also not without influence (Expt. No. 82, *b*); on this account the method seems to be applicable only, if the standardizing of the cyanide of potassium and the actual analyses are performed under very similar circumstances.

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[*] Polytechn. Centralbl. 1859, 1313.

[†] Annal. d. Chem. u. Pharm. 94, 198; Fr. Mohr's Lehrbuch der Titrirmethode, 2, 91.

[‡] Annal. d. Chem. u. Pharm. 95, 118.

[§] In six experiments, in which he had purposely added different quantities of carbonate of ammonia, Fleck used for 100 c. c. copper solution, in the minimum 15·2, in the maximum 15·75, in the mean 15·46 c. c. cyanide of potassium solution.

§ 120.

6. TEROXIDE OF BISMUTH.

a. Solution.

Metallic bismuth, the teroxide, and all other compounds of that metal, are dissolved best in nitric acid, more or less diluted. It must be borne in mind that hydrochloric acid solutions of bismuth, if concentrated, cannot be evaporated without loss of chloride of bismuth.

b. Determination.

Bismuth is weighed in the form of *teroxide*, of *chromate*, of *sulphide*, or in the *metallic state*. The compounds of bismuth are converted into teroxide by ignition, by precipitation as basic carbonate, or by repeated evaporation of the nitrate solution. These are sometimes preceded by separation as sulphide. The determination as metallic bismuth is frequently preceded by precipitation as sulphide or as basic chloride.

We may convert into

1. TEROXIDE OF BISMUTH.

a. By Precipitation as Carbonate of Teroxide of Bismuth.

All compounds of bismuth which dissolve in nitric acid to nitrate, *no* other acid remaining in the solution.

b. By Ignition.

α. Salts of bismuth with readily volatile oxygen acids.

β. Salts of bismuth with organic acids.

c. By Evaporation.

Bismuth in nitric acid solution.

d. By Precipitation as Tersulphide of Bismuth.

All compounds of bismuth without exception.

2. CHROMATE OF TEROXIDE OF BISMUTH.

All compounds named in 1, *a*.

3. SULPHIDE OF BISMUTH.

The compounds of bismuth without exception.

4. BASIC CHLORIDE OF BISMUTH.

All compounds of bismuth.

5. METALLIC BISMUTH.

The oxide and its salts, the sulphide, and the basic chloride.

1. *Determination of Bismuth as Teroxide.*

a. By Precipitation as Carbonate of Teroxide of Bismuth.

Mix the solution of bismuth with carbonate of ammonia in *very slight* excess, and heat for some time nearly to boiling; filter, dry the precipitate, and ignite in the manner directed § 116, 1 (Ignition of carbonate of lead); the process of ignition serves to convert the carbonate into the pure teroxide of bismuth. Should the solution be too concentrated, dilute with water, previously to the addition of carbonate of ammonia; whether the dilution leads to the precipitation of basic nitrate of bismuth or not, is a matter of perfect indifference. For the properties of the precipitate and residue, see § 86.

The method gives accurate results, though generally a trifle too low, owing to the circumstance that carbonate of teroxide of bismuth is not absolutely insoluble in carbonate of ammonia.

Were you to attempt to precipitate bismuth, by means of carbonate of ammonia, from solutions containing sulphuric acid or hydrochloric acid, you would obtain incorrect results, since with the basic carbonate, basic sulphate or basic chloride would be precipitated, which are not decomposed by excess of carbonate of ammonia. Were you to filter off the precipitate without warming, a considerable loss would be sustained, as the whole of the basic carbonate would not have been separated (Expt. No. 83).

b. By Ignition.

α. Compounds like the carbonate or nitrate of teroxide of bismuth are ignited in a porcelain crucible until their weight remains constant.

β. Compounds of teroxide of bismuth with organic acids are treated like the corresponding compounds of oxide of copper (§ 119, 1, *d*).

c. By Evaporation.

The solution of the nitrate is evaporated, in a porcelain dish on the water-bath, till the neutral salt remains in syrupy solution;—add water, loosen the white crust that is formed with a glass rod from the sides, evaporate again on a water-bath, reprecipitate with water, and repeat the whole operation three or four times. After the dry mass on the water-bath has ceased to smell of nitric acid, it is allowed to cool thoroughly, and then treated with cold water containing a little nitrate of ammonia (1 in 500); after the residue and fluid have been a short time together, filter, wash with the weak solution of nitrate of ammonia, dry and ignite (§ 53). Results very satisfactory (J. Löwe *).

d. By Precipitation as Tersulphide of Bismuth.

Dilute the solution with water slightly acidulated with acetic acid (to prevent the precipitation of a basic salt), and precipitate with sulphuretted hydrogen water or gas; allow the precipitate to subside, and test a portion of the supernatant fluid with *sulphuretted hydrogen water*; if it remains clear, which is a sign that the bismuth is completely precipitated, filter (the filtrate should smell strongly of H S), and wash the precipitate with water containing sulphuretted hydrogen. Or mix with ammonia until the free acid is neutralized, and then add sulphide of ammonium in excess.

The washed precipitate may now be weighed in three different forms, viz., as sulphide, as metal, or as oxide. The treatment in the two former cases will be described in 3 and 5: in the latter case proceed as follows:—

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* Journ. f. prakt. Chem. 74, 344.

Spread the filter out on a glass plate and remove the precipitate to a vessel by means of a jet of water from the wash-bottle—or, if this is not practicable, put the precipitate and filter together into the vessel—and heat gently with moderately strong nitric acid until complete decomposition is effected; the solution is then diluted with water slighly acidulated with acetic or nitric acid, and filtered, the filter being washed with the acidulated water; the filtrate is then finally precipitated as directed in *a.*

2. *Determination of Bismuth as Chromate of Teroxide.* (J. Lowe.*)

Pour the solution of teroxide of bismuth, which must be as neutral as possible, and must, if necessary, be first freed from the excess of nitric acid by evaporation on the water-bath, into a warm solution of pure bichromate of potassa in a porcelain dish, with stirring, and take care to leave the alkaline chromate slightly in excess. Rinse the vessel which contained the solution of bismuth with water containing nitric acid into the porcelain dish. The precipitate formed must be orange-yellow, and dense throughout; if it is flocculent, and has the color of the yolk of an egg, this is a sign that there is a deficiency of chromate of potassa; in which case add a fresh quantity of this salt, taking care, however, to guard against too great an excess, and boil until the precipitate presents the proper appearance. Boil the contents of the dish for ten minutes, with stirring; then wash the precipitate, first by repeated boiling with water and decantation on to a weighed filter, at last thoroughly on the latter with boiling water; dry at about 120°, and weigh. For the properties and composition of the precipitate, see § 86. Results very satisfactory.

3. *Determination of Bismuth as Sulphide.*

Precipitate the bismuth as sulphide according to 1, *d.* If the precipitate contains sulphur, extract the later by boiling with solution of sulphite of soda, or by treatment with bisulphide of carbon (compare the determination of mercury as sulphide, § 118, 3), collect on a weighed filter, dry at 100°, and weigh.

The drying must be conducted with caution. At first the precipitate loses weight, by the evaporation of water, then it gains weight, from the absorption of oxygen. Hence you should weigh every half-hour, and take the lowest weight as the correct one. Compare Expt. No. 58. Properties and composition, § 86, *e.*

The sulphide of bismuth cannot be conveniently converted into the metallic state by ignition in hydrogen, as its complete decomposition is a work of considerable time. As regards reduction with cyanide of potassium, see 5.

4. *Precipitation of Bismuth as Basic Chloride.*

The precipitation of bismuth as basic chloride, and the reduction of the latter with cyanide of potassium, is recommended by H. Rose.† The process is conducted as follows:—nearly neutralize any large excess of acid that may be present with potassa, soda, or ammonia, add chloride of sodium in sufficient quantity (if hydrochloric acid is not already present), and then a rather large quantity of water. After allowing to stand some time, test whether a portion of the clear supernatant fluid is rendered turbid by a further addition of water; and then, if required, add water to the whole till the precipitation is complete. Finally, filter the precipitate, wash completely with cold water, dry and fuse with cyanide of potassium as directed below (5). Results accurate.

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* Journ. f. prakt. Chem. 67, 464.

† Pogg. Annal. 110, 425.

5. *Determination of Bismuth as Metal.*

The oxide, sulphide, or basic chloride that are to be reduced are fused in a large porcelain crucible with five times their quantity of ordinary cyanide of potassium. In the case of oxide and basic chloride, the reduction is completed in a short time at a gentle heat; sulphide, on the other hand, requires longer fusion and a higher temperature. The operation has been successful, if on treatment with water metallic grains are obtained. These grains are first washed completely and rapidly with water, then with weak, and lastly with strong spirit, dried and weighed. If you have been reducing the sulphide, and on treating the fused mass with water a black powder (a mixture of bismuth with sulphide of bismuth) is visible, besides the metallic grains, it is necessary to fuse the former again with cyanide of potassium.

It sometimes happens that the crucible is attacked, and particles of porcelain are found mixed with the metallic bismuth; to prevent this from spoiling the analysis, weigh the crucible together with a small dry filter before the experiment, collect the metal on the filter, dry and weigh the crucible with the filter and bismuth again. Results good (H. ROSE *).

§ 121.

7. OXIDE OF CADMIUM.

a. Solution.

Cadmium, its oxide, and all the other compounds insoluble in water, are dissolved in hydrochloric acid or in nitric acid.

b. Determination.

Cadmium is weighed either in the form of *oxide*, or in that of *sulphide* (§ 87).

We may convert into

1. OXIDE OF CADMIUM.

a. By Precipitation.	*b. By Ignition.*
The compounds of cadmium which are soluble in water; the insoluble compounds, the acid of which is removed upon solution in hydrochloric acid; salts of cadmium with organic acids.	Salts of cadmium with readily volatile or easily decomposable inorganic oxygen acids.

2. SULPHIDE OF CADMIUM.

All compounds of cadmium without exception.

1. *Determination as Oxide of Cadmium.*

a. By Precipitation.

Precipitate with carbonate of soda or potassa, wash the precipitated

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[*] Pogg. Annal. 91, 104, and 110, 136.

carbonate of cadmium, and convert it, by ignition, into the state of pure oxide. The precipitation is conducted as in the case of zinc, § 108, 1, *a*. The oxide of cadmium which adheres to the filter may easily be reduced and volatilized; it is therefore necessary to be cautious. In the first place choose a thin filter, transfer the dried precipitate as completely as possible to the crucible, replace the filter in the funnel, and moisten it with nitrate of ammonia solution, allow to dry, and then burn carefully in a coil of platinum wire. Let the ash fall into the crucible containing the mass of the precipitate, ignite carefully, avoid the action of reducing gases, and finally weigh. For the properties of the precipitate and the residue, see § 87. Results good.

b. By Ignition.

Same process as for zinc, § 108, 1, *c*.

2. *Determination as Sulphide of Cadmium.*

Neutral or acid solutions are precipitated with sulphuretted hydrogen water or gas, which must be used in sufficient excess. The presence of a considerable quantity of free hydrochloric or nitric acid may—especially if the solution is not enough diluted—prevent complete precipitation, hence such an excess should be avoided, and the clear supernatant fluid should in all cases be tested, by the addition of a relatively large amount of sulphuretted hydrogen water to a portion, before being filtered. Alkaline solutions of cadmium may be precipitated with sulphide of ammonium. If the sulphide of cadmium is free from admixed sulphur, it may be at once collected on a weighed filter, dried at 100°, and weighed; if, on the contrary, it contains free sulphur, it may be purified by boiling with a solution of sulphite of soda, or by treatment with bisulphide of carbon (see Sulphide of mercury, § 118, 3). Results accurate. The precipitation of sulphur may occasionally be obviated by adding to the cadmium solution cyanide of potassium till the precipitate first formed is redissolved, and then precipitating this solution with sulphuretted hydrogen.

If the sulphide of cadmium is not to be weighed as such, warm it, together with the filter, with moderately strong hydrochloric acid, till the precipitate has dissolved and the odor of sulphuretted hydrogen is no longer perceptible, filter and precipitate the solution as in 1, *a*, after having removed the excess of free acid for the most part by evaporation.

Supplement to the Fifth Group.

§ 122.

8. PROTOXIDE OF PALLADIUM.

Protoxide of palladium is converted, for the purpose of estimation, into the *metallic state*; or—in many separations—into *double chloride of palladium and potassium.*

1. *Determination as Palladium.*

a. Neutralize the solution of protochloride of palladium almost completely with carbonate of soda, mix with a solution of cyanide of mercury; and digest the mixture for some time. A yellowish-white precipitate of protocyanide of palladium will subside; from dilute solutions, only after the lapse of some time. Wash this precipitate, dry, and ignite; weigh the reduced metal obtained. If the solution contains nitrate of protoxide, evaporate it first with hydrochloric acid to dryness; as otherwise the precipitate obtained deflagrates upon ignition (Wollaston).

b. Mix the solution of the protochloride or nitrate of protoxide of palladium with formiate of soda or potassa, and warm until no more carbonic acid escapes. The palladium precipitates in brilliant scales (Döbereiner).

c. Precipitate the acid solution of palladium with sulphuretted hydrogen, filter, wash with boiling water, roast, and either convert the basic sulphate of protoxide of palladium formed into pure metal, by ignition over the blast gas-lamp, or dissolve it in hydrochloric acid, and precipitate as in *a.*

Exposed to a moderate red heat metallic palladium becomes covered with a film varying from violet to blue, but at a higher temperature it recovers its lustre; this tarnishing and recovery of the metallic lustre is not attended with any perceptible difference of weight. Palladium requires the very highest degree of heat for its fusion. It dissolves readily in nitrohydrochloric acid, with difficulty in pure nitric acid, more easily in nitric acid containing nitrous acid, with difficulty in boiling concentrated sulphuric acid.

2. *Determination as Double Chloride of Palladium and Potassium.*

Evaporate the solution of chloride of palladium with chloride of potassium and nitric acid to dryness, and treat the mass when cold with alcohol of ·833 sp. gr., in which the double salt is insoluble. Collect on a weighed filter, dry at 100°, and weigh. Results a little too low, as traces of the double salt pass away with the alcohol washings (Berzelius).

The double chloride of palladium and potassium consists of microscopic octahedra; it presents the appearance of a vermilion, or, if the crystals are somewhat larger, of a brown powder. It is very slightly soluble in cold water; it is almost insoluble in cold spirit of the above strength. It contains 26·701% palladium.

SIXTH GROUP.

Teroxide of Gold—Binoxide of Platinum—Teroxide of Antimony—Binoxide of Tin—Protoxide of Tin—Arsenious and Arsenic Acids—(Molybdic Acid).

§ 123.

1. Teroxide of Gold.

a. Solution.

Metallic gold, and all compounds of gold insoluble in water, are warmed with hydrochloric acid, and nitric acid is gradually added until complete solution is effected; or they are repeatedly digested with strong chlorine water. The latter method is resorted to more especially in cases where the quantity of gold to be dissolved is small, and mixed with foreign oxides, which it is wished to leave undissolved.

b. Determination.

Gold is always weighed in the *metallic state.* The compounds are brought into this form, either by ignition or by precipitation, as gold, or sulphide of gold. See Cupellation, § .

We convert into

METALLIC GOLD.

a. By Ignition.	*b. By Precipitation as Metalli Gold.*
All compounds of gold which contain no fixed acid.	All compounds of gold witho exception in cases where *a* is ina plicable.

c. By Precipitation as Tersulphide of Gold.

This method serves to effect the separation of gold from certain other metals which may be mixed with it in a solution.

Determination as Metallic Gold.

a. By Ignition.

Heat the compound, in a covered porcelain crucible, very gently at first, but finally to redness, and weigh the residuary pure gold. For properties of the residue, see § 88. The results are most accurate.

b. By Precipitation as Metallic Gold.

α. The solution is free from Nitric Acid.

Mix the solution with a little hydrochloric acid, if it does not already contain some of that acid in the free state, and add a clear solution of sulphate of protoxide of iron in excess; heat gently for a few hours until the precipitated fine gold powder has completely subsided; filter, wash, dry, and ignite according to § 52. A porcelain dish is a more appropriate vessel to effect the precipitation in than a beaker, as the heavy fine gold powder is more readily rinsed out of the former than out of the latter. The results are accurate.

β. The solution of Gold contains Nitric Acid.

Evaporate the solution, on a water-bath, to the consistence of syrup, adding from time to time hydrochloric acid; dissolve the residue in water containing hydrochloric acid, and treat the solution as directed in *α*. It will sometimes happen that the residue does not dissolve to a clear fluid, in consequence of a partial decomposition of the terchloride of gold into protochloride and metallic gold; however, this is a matter of perfect indifference.

γ. In cases where it is wished to avoid the presence of iron in the filtrate, the gold may be reduced by means of oxalic acid. To this end, the dilute solution—freed previously, if necessary, from nitric acid, in the manner directed in *β*—is mixed, in a beaker, with oxalic acid, or with oxalate of ammonia in excess, some hydrochloric acid added (if that acid is not already present in the free state), and the vessel, covered with a glass plate, is kept standing for two days in a moderately warm place. At the end of that time, the whole of the gold will be found to have separated in small yellow scales, which are collected on a filter, washed, dried, and ignited. If the gold solution contains a large excess of hydrochloric acid, the latter should be for the most part evaporated, before the solution is diluted and the oxalic acid added. If the gold solution contains chlorides of alkali metals, it is necessary to dilute largely, and allow to stand for a long time, in order to effect complete precipitation (H. ROSE).

c. By Precipitation as Tersulphide of Gold.

Sulphuretted hydrogen gas is transmitted in excess through the dilute solution; the precipitate formed is speedily filtered off, without heating, washed, dried, and ignited in a porcelain crucible. For the properties of the precipitate, see § 88. The results are accurate.

§ 124.

2. BINOXIDE OF PLATINUM.

a. Solution.

Metallic platinum, and the compounds of platinum which are insoluble in water, are dissolved by digestion, at a gentle heat, with nitrohydrochloric acid.

b. Determination.

Platinum is invariably weighed in the *metallic state*, to which condition its compounds are brought, either by precipitation as bichloride of platinum and chloride of ammonium, bichloride of platinum and chloride of potassium, or bisulphide of platinum, or by ignition, or by precipitation with reducing agents. All compounds of platinum, without exception, may, in most cases, be converted into platinum by either of these methods. Which is the most advantageous process to be pursued in special instances, depends entirely upon the circumstances. The reduction of compounds of platinum to the metallic state by simple ignition is preferable to the other methods, in all cases where its application is admissible. The precipitation as bisulphide of platinum is resorted to exclusively to effect the separation of platinum from other metals.

Determination as Metallic Platinum.

a. By Precipitation as Bichloride of Platinum and Chloride of Ammonium.

The solution must be concentrated if necessary by evaporation on a water-bath. Mix, in a beaker, with ammonia until the excess of acid (that is, supposing an excess of acid to be present) is *nearly* saturated; add chloride of ammonium in excess, and mix the fluid with a pretty large quantity of absolute alcohol.

Cover the beaker now with a glass plate, and let it stand for twenty-four hours, after which filter on an unweighed filter, wash the precipitate with spirit of wine of about 80 per cent., till the substances to be separated are removed, and dry carefully.

Introduce the dry precipitate, wrapped up in the filter, into a weighed porcelain crucible, put on the lid, and apply a very gentle heat for some time, until no more fumes of chloride of ammonium escape; now remove the lid, place the crucible obliquely (§ 52), and let the filter burn. Apply finally an intense heat for some time, and then weigh. In the case of large quantities this final ignition is advantageously conducted in a stream of hydrogen (§ 108, fig. 47, p. 181), or with addition of oxalic acid, in order to be quite sure of effecting complete decomposition. For the properties of the precipitate and residue, see § 89. The results are satisfactory, though generally a little too low, as the bichloride of platinum and chloride of ammonium is not altogether insoluble in spirit of wine (Expt. No. 16); and as the fumes of chloride of ammonium evolved during the first stage of the process of ignition are liable to carry away traces of the yet undecomposed double chloride, if the application of heat is not conducted with the greatest possible care.

If the precipitated bichloride of platinum and chloride of ammonium were weighed in that form, the results would be inaccurate, since, as I have convinced myself by direct experiments, it is impossible to completely free the double chloride, by washing with spirit of wine, from all traces of the chloride of ammonium thrown down in conjunction with it, without dissolving, at the same time, a considerable portion of the double chloride. As a general rule, the results obtained by weighing the bichloride of platinum and chloride of ammonium in that form are one or two per cent. too high.

b. By Precipitation as Bichloride of Platinum and Chloride of Potassium.

Mix the solution of the compound under examination in a beaker, with potassa, until the greater part of the excess of acid (if there be any) is neutralized; add chloride of potassium slightly in excess, and finally a pretty large quantity of absolute alcohol; should your solution of platinum be very dilute, you must concentrate it previously to the addition of the alcohol. After twenty hours, collect the precipitate upon a weighed filter, wash with spirit of wine of 70 per cent., dry thoroughly at 100°, and weigh. Now put a portion of the dried precipitate into a weighed bulb-tube, and clean the tube part of the latter with a feather; then weigh the tube again, to ascertain the exact amount of bichloride of platinum and chloride of potassium which it contains. Connect the tube now with an apparatus evolving dry hydrogen gas, and heat its contents to redness, until no more hydrochloric acid fumes are evolved, which you may readily ascertain by holding a glass rod moistened with ammonia to the opening of the tube. Allow to cool, remove the tube from the apparatus, fill it with water, decant the solution of chloride of potassium cautiously, wash the residuary platinum carefully, dry the tube thoroughly (by heating it in the stream of hydrogen gas), and weigh. Subtract from the weight found the original weight of the empty tube, and calculate from the remainder (the weight of the residuary platinum in the tube) the amount of platinum contained in the whole precipitate.

For the properties of the precipitate and residue, see § 89.

The results are more accurate than those obtained by method *a*, since, on the one hand, the bichloride of platinum and chloride of potassium is more insoluble in spirit of wine than the corresponding ammonium salt; and, on the other hand, loss of substance is less likely to arise during the process of ignition than is the case in method *a*. The results would be less accurate were the ignition effected simply in a crucible, instead of in a current of hydrogen gas, since in that case complete decomposition will not ensue, at all events not if the amount of substance acted upon is at all considerable. To weigh the bichloride of platinum and chloride of potassium in that form would not be practicable, as it is impossible to remove, by washing with spirit of wine, all traces of the chloride of potassium thrown down along with it, without at the same time dissolving a portion of the double chloride. The reduction may also be effected with the apparatus described § 108 (fig. 47, p. 181), or in a porcelain boat, contained in a wide glass tube, instead of in a bulb-tube.

c. By Precipitation as Bisulphide of Platinum.

Precipitate the solution with sulphuretted hydrogen water or gas, according to circumstances, heat the mixture to incipient ebullition, filter, wash the precipitate, dry, and ignite according to § 52. For the properties of the precipitate and residue, see § 89. The results are accurate.

d. By Ignition.

Heat in a covered porcelain crucible, very gently at first, but finally to redness, and weigh the residuary pure platinum. For the properties of the residue, see § 89. The results are most accurate.

e. By Precipitation with Reducing Agents.

Various reducing agents may be employed to precipitate platinum from its solutions in the metallic state. The reduction is very promptly effected by sulphate of iron and potassa or soda (the protosesquioxide of iron being removed by subsequent addition of hydrochloric acid, HEMPEL), or by pure zinc (the excess of which is removed by hydrochloric acid); somewhat more slowly, and only with application of heat, by alkaline formiates. Nitrate of suboxide of mercury also precipitates the whole of the platinum from solution of the bichloride; upon igniting the brown precipitate obtained, fumes of subchloride of mercury escape, and metallic platinum remains.

§ 125.

3. TEROXIDE OF ANTIMONY.

a. Solution.

Teroxide of antimony, and the compounds of that metal which are insoluble in water, or are decomposed by that agent, are dissolved in more or less concentrated hydrochloric acid. Metallic antimony is dissolved best in nitrohydrochloric acid. The ebullition of a hydrochloric acid solution of terchloride of antimony is attended with volatilization of traces of the latter; the concentration of a solution of the kind by evaporation involves accordingly loss of substance. Solutions so highly dilute as to necessitate a recourse to evaporation must therefore previously be supersaturated with potassa. Hydrochloric acid solutions of teroxide of antimony, which it is intended to dilute with water, must previously be mixed with tartaric acid, to prevent the separation of basic salt. In diluting an acid solution of antimonic acid in hydrochloric acid, the water must not be added gradually and in small quantities at a time, which would make the fluid turbid, but in sufficient quantity at once, which will leave the fluid clear.

b. Determination.

Antimony is weighed either as *tersulphide* or as *metallic antimony*, or as *antimoniate of teroxide* ($Sb\ O_4$); or it is estimated by volumetric analysis.

The oxides of antimony, and their salts with readily volatile or decomposable oxygen acids, may be converted into antimoniate of teroxide by simple ignition. Antimony in solution is almost invariably first precipitated as sulphide, which is then, with the view of estimation, converted into anhydrous sulphide, into the metallic state, or into antimoniate of teroxide, or determined volumetrically. The method of estimating antimony with a standard solution of iodine can only be employed when it is contained in the solution as pure teroxide. Hence it is only capable of limited application.

1. *Precipitation as Sulphide of Antimony.*

Add to the antimony solution hydrochloric acid, if not already present, then tartaric acid, and dilute with water, if necessary. Introduce the clear fluid into a flask, closed with a doubly perforated cork; through one of the perforations passes a tube, bent outside at a right angle, which nearly extends to the bottom of the flask; through the other perforation passes another tube, bent outside twice at right angles, which reaches only a short way into the flask; the outer end of this tube dips slightly under water. Conduct through the first tube sulphuretted hydrogen gas, until it predominates strongly; put the flask in a moderately warm place, and after some time conduct carbonic acid into the fluid, until the excess of the other gas is almost completely removed; filter now without intermission through a weighed filter, wash the precipitate rapidly and thoroughly with water mixed with a few drops of sulphuretted hydrogen water, dry at 100°, and weigh. The precipitate so weighed always retains some water, and may, besides, contain free sulphur; in fact, it always contains the latter in cases where the antimony solution, besides teroxide or terchloride, contains antimonic acid or pentachloride of antimony, since the precipitation under these circumstances is preceded by a reduction of the higher oxide or chloride to teroxide or terchloride, accompanied by separation of sulphur. (H. ROSE.) A further examination of the precipitate is accordingly indispensable.

To this end, treat a sample of the weighed precipitate with strong hydrochloric acid. If

a. The sample dissolves to a clear fluid, this is a proof that the precipitate only contains $Sb\ S_3$; but if

b. Sulphur separates, this shows that free sulphur is present.

In case *a*, the greater portion of the dried precipitate is weighed in a porcelain boat, which is then inserted into a sufficiently wide glass tube, about 2 decimetres long; a slow current of dry carbonic acid is transmitted through the latter, and the boat cautiously heated by means of a lamp, moved to and fro under it, until the orange precipitate becomes black; this operation serves to expel the whole of the water present. The precipitate is then allowed to cool in the current of carbonic acid, and weighed; from the amount found, the total quantity of anhydrous sulphide of antimony contained in the entire precipitate is ascertained by a simple calculation. The results are accurate. Expt. No. 84 gave 99·24 instead of 100. But if the precipitate is simply dried at 100°, the results are about 2 per cent. too high—see the same experiment. For the properties of the precipitate, see § 90.

In case *b*, the precipitate is subjected to the same treatment as in *a*, with this difference only, that the contents of the boat are heated much more intensely, and the process is continued until no more sulphur is expelled. This removes the whole of the admixed sulphur; the residue consists of pure tersulphide of antimony. It must be completely soluble in fuming hydrochloric acid on heating.

According to BUNSEN it is best to convert the sulphide of antimony into antimoniate of teroxide (see 2).

The method (described in § 148) of estimating the sulphur in the precipitate dried at 100°, and calculating the antimony from the difference, does not give accurate results, since the precipitate, besides antimony and sulphur, contains also water. In cases, therefore, where this indirect method is resorted to, the water must first be expelled, as directed in *a*.

The antimony may also be determined in the direct way, in the precipitate dried at 100°. To this end, an aliquot part of it is weighed in a bulb-tube, hydrogen gas transmitted through the latter, and a very gentle heat applied, which is gradually increased, until no more sulphuretted hydrogen escapes. It is hardly possible, however, to avoid a slight loss of antimony in this process, as a small portion of that body is but too apt to be mechanically carried away by the hydrogen gas.

For the method of estimating the antimony in the sulphide volumetrically and indirectly, see 3, *a*.

2. *Determination as Antimoniate of Teroxide.*

a. In the case of teroxide of antimony or a compound of the same with an easily volatile or decomposable oxygen acid, evaporate carefully with nitric acid, and ignite finally for some time till the weight is constant. The experiment may be safely made in a platinum crucible. With antimonic acid, the evaporation with nitric acid is unnecessary.

b. If sulphide of antimony is to be converted into antimoniate of teroxide, one of the two following methods given by BUNSEN[*] is employed:—

α. Moisten the dry sulphide of antimony with a few drops of nitric acid of 1·42 sp. gr., then treat, in a weighed porcelain crucible, with concave lid, with 8—10 times the quantity of fuming nitric acid,[†] and let the acid gradually evaporate on the water-bath. The sulphur separates at first as a fine powder, which, however, is readily and completely oxidized during the process of evaporation. The white residual mass in the crucible consists of antimonic acid and sulphuric acid, and may by ignition be converted, without loss, into antimoniate of teroxide of antimony. If the sulphide of antimony contains a large excess of free sulphur, this must first be removed by washing with bisulphide of carbon (see β at the end), before proceeding to oxidation.

β. Mix the sulphide of antimony with 30—50 times its quantity of pure oxide of mercury,[‡] and heat the mixture gradually in an open porcelain crucible. As soon as oxidation begins, which may be known by the sudden evolution of gray mercurial fumes, moderate the heat. When the evolution of mercurial fumes diminishes raise the temperature again, always taking care, however, that no reducing gases come in contact with the contents of the crucible. Remove the last traces of oxide of mercury over the blast gas-lamp, then weigh the residual fine white powder of antimoniate of teroxide of antimony. As oxide of mercury generally leaves a trifling fixed residue upon ignition, the amount of this should be determined once for all, the oxide of mercury added approximately weighed, and the corresponding amount of fixed residue deducted from the antimoniate of teroxide of antimony. The volatilization of the oxide of mercury proceeds much more rapidly when effected in a platinum crucible, instead of a porcelain one. But, if a platinum crucible is employed, it must be effectively protected from the action of antimony upon it, by a *good lining* of oxide of mercury.* If the sulphide of antimony contains free sulphur, this must first be removed by washing with bisulphide of carbon, before the oxidation can be proceeded with, since otherwise a slight deflagration is unavoidable. The bisulphide of carbon used may be very easily rectified, and then used again, so that the washing of a precipitate may be effected with as little as 10—15 grammes of bisulphide of carbon.

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[*] Annal. d. Chem. u. Pharm. 106, 3.

[†] Nitric acid of 1·42 sp. gr. is not suitable for this purpose, as its boiling point is almost 10° above the fusing point of sulphur, whereas fuming nitric acid boils at 86°, consequently below the fusing point of sulphur. With nitric acid of 1·42 sp. gr., therefore, the separated sulphur fuses and forms drops, which obstinately resist oxidation.

[‡] It is best to use that prepared in the wet way.

3. *Volumetric Methods.*

The proposals under this head are based, either,

a. Upon the decomposition of the sulphide on boiling with hydrochloric acid, and the determination of the sulphuretted hydrogen evolved. (R. SCHNEIDER.†)

b. Upon the oxidation of the teroxide with permanganate (KESSLER ‡).

a. Volumetric Estimation by determining the Sulphuretted Hydrogen given up by the Sulphide.

Both tersulphide and pentasulphide yield under the action of boiling hydrochloric acid 3 eq. of sulphuretted hydrogen for every 1 eq. of antimony. Hence, if the amount of the gas evolved under such circumstances is estimated, the amount of antimony is known.

For decomposing the sulphide and absorbing the gas the same apparatus serves as BUNSEN employs for his iodimetric analyses (§ 130, fig. 51). The size of the boiling flask should depend on the quantity of sulphide: for quantities up to 0·4 grm. SbS_3, a flask of 100 c. c. is large enough; for ·4—1·0 grm., use a 200 c. c. flask. The body of the flask should be spherical, the neck rather narrow, long, and cylindrical. If the sulphide of antimony is on a filter, put both together into the flask. The hydrochloric acid should not be too concentrated.

The determination of the sulphuretted hydrogen is best conducted according to the method given in § 148, *b*. The results obtained by SCHNEIDER are satisfactory.

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* This is effected best, according to Bunsen, in the following way: Soften the sealed end of a common test tube before the glass-blower's lamp; place the softened end in the centre of the platinum crucible, and blow into it, which will cause it to expand and assume the exact form of the interior of the crucible. Crack off the bottom of the little flask so formed, and smooth the sharp edge cautiously by fusion. A glass is thus obtained, open at both ends, which exactly fits the crucible. To effect the lining by means of this instrument, fill the crucible loosely with oxide of mercury up to the brim, then force the glass gradually and slowly down to the bottom of the crucible, occasionally shaking out the oxide of mercury from the interior of the glass. The inside of the crucible is thus covered with a layer of oxide of mercury ½—1 line thick, which, after the removal of the glass, adheres with sufficient firmness, even upon ignition.

† Pogg. Annal. 110, 634. ‡ Zeitschrift f. anal. Chem. 2, 383.

If the precipitate contains chloride of antimony, the results are of course false, and this would actually be the case if on precipitation with sulphuretted hydrogen the addition of tartaric acid were omitted.

b. Volumetric Determination with Permanganate of Potash.

In the absence of organic matter, heavy metallic oxides, and other bodies which are detrimental to the reaction, dissolve the substance containing teroxide of antimony, at once in hydrochloric acid. The solution should contain not less than $\frac{1}{8}$ of its volume of hydrochloric acid of 1·12 sp. gr.

The permanganate solution, which may contain about 1·5 grm. of the crystallized salt in a litre, is added to permanent reddening. The end-reaction is exact, and the oxidation of the teroxide of antimony to antimonic acid goes on uniformly, although the degree of dilution may vary, provided the above relation between hydrochloric acid and water is kept up. It is not well that the hydrochloric acid should exceed $\frac{1}{3}$ of the volume of the fluid, as in that case the end-reaction would be too transitory. Tartaric acid, at least in the proportion to teroxide of antimony in which it exists in tartar emetic, does not interfere with the reaction. Hence the permanganate may be standardized by the aid of solution of tartar emetic of known strength.

If the direct determination of the hydrochloric acid solution is not practicable, precipitate it with sulphuretted hydrogen. Wash the precipitate, transfer it, together with the filter, to a small flask; treat it with a sufficiency of hydrochloric acid, dissolve by digestion on the water-bath, add a sufficient quantity of a nearly saturated solution of chloride of mercury in hydrochloric acid of 1·12 sp. gr. to remove the sulphuretted hydrogen, make the fluid up to a certain volume, allow to settle, and use a measured portion of the *perfectly clear* solution for the experiment.

§ 126.

4. PROTOXIDE OF TIN, and 5. BINOXIDE OF TIN.

a. Solution.

In dissolving compounds of tin soluble in water, a little hydrochloric acid is added to insure a clear solution. Nearly all the compounds of tin insoluble in water dissolve in hydrochloric acid or in aqua regia. The hydrate of metastannic acid may be dissolved by boiling with hydrochloric acid, decanting the fluid, and treating the residue with a large proportion of water. Ignited binoxide of tin, and compounds of the binoxide insoluble in acids, are prepared for solution in hydrochloric acid, by reducing them to the state of a fine powder, and fusing in a silver crucible with hydrate of potassa, or soda, in excess. Metallic tin is dissolved best in aqua regia; it is generally determined, however, by converting it into binoxide, without previous solution. Acid solutions of binoxide of tin, which contain hydrochloric acid, or a chloride, cannot be concentrated by evaporation, not even after the addition of nitric acid or sulphuric acid, without volatilization of bichloride of tin taking place.

b. Determination.

Tin is weighed in the form of *binoxide*, into which it is converted, either by the agency of nitric acid, or by precipitation as hydrated binoxide, or by precipitation as sulphide.

A great many volumetric methods of estimating tin have been proposed. They all depend on obtaining the tin in solution in the condition of protochloride, and converting this into bichloride either in alkaline or acid solution. A few only yield satisfactory results.

We may convert into

Binoxide of Tin.

a. By the agency of Nitric Acid.

Metallic tin, and those compounds of tin which contain no fixed acid, provided no compounds of chlorine be present.

b. By Precipitation as Hydrated Binoxide.

All compounds of tin containing volatile acids, provided no non-volatile organic substances nor sesquioxide of iron be present.

c. By Precipitation as Sulphide.

All compounds of tin without exception.

In methods *a* and *c*, it is quite indifferent whether the tin is present in the state of protoxide or in that of binoxide. The method *b* requires the tin to be present in the state of binoxide. The volumetric methods may be employed in all cases; but the estimation is simple and direct only where the tin is in solution as protochloride and free from other oxidizable bodies, or can readily be brought into this state. For the methods of determining the protoxide and binoxide in presence of each other, I refer to Section V.

1. *Determination of Tin as Binoxide.*

a. By Treating with Nitric Acid.

This method is resorted to principally to convert the metallic tin into binoxide. For this purpose the finely-divided metal is put into a capacious flask, and moderately concentrated pure nitric acid (about 1·3 sp. gr.) gradually poured over it; the flask is covered with a watch-glass. When the first tumultuous action of the acid has somewhat abated, a gentle heat is applied until the binoxide formed appears of a pure white color, and further action of the acid is no longer perceptible. The contents of the flask are then transferred to a porcelain dish and evaporated on a water-bath to dryness, water is then added, and the precipitate is collected on a filter, washed, till the washings scarcely redden litmus paper, dried, ignited, and weighed. The ignition is effected best in a small porcelain crucible, according to the directions given in § 53; still a platinum crucible may also be used. A simple red heat is not sufficient to drive off all the water; the ignition must therefore be finished over a gas blast-lamp. Compounds of tin which contain no fixed substances may be converted into binoxide by treating them in a porcelain crucible with nitric acid, evaporating to dryness, and igniting the residue. If sulphuric acid be present, the expulsion of that acid may be promoted, in the last stages of the process, by carbonate of ammonia, as in the case of bisulphate of potassa (§ 97); here also the heat must be increased as much as possible at the end. For the properties of the residue, see § 91. The results are accurate.

b. By Precipitation as Hydrate of Binoxide.

The application of this method presupposes the whole of the tin to be present in the state of binoxide or bichloride. Therefore, if a solution contains protoxide, either mix with chlorine water, or conduct chlorine gas into it, or heat gently with chlorate of potassa, until the conversion of the protoxide into binoxide is effected. When this has been done, add ammonia until a permanent precipitate just begins to form, and then hydrochloric acid, drop by drop, until this precipitate is completely redissolved; by this means a large excess of hydrochloric acid in the solution will be avoided. Add to the fluid so prepared a concentrated solution of nitrate of ammonia (or sulphate of soda), and apply heat for some time, whereupon the whole of the tin will precipitate as hydrate of binoxide. Decant three times on to a filter, then collect the precipitate on the latter, wash thoroughly, dry, and ignite. To make quite sure that the whole of the tin has separated, you need simply, before proceeding to filter, add a few drops of the clear supernatant fluid to a hot solution of nitrate of ammonia, or sulphate of soda, when the formation or nonformation of a precipitate will at once decide the question.

This method, which we owe to J. LOWENTHAL, has been repeatedly tested by him in my own laboratory,* is easy and convenient, and gives very accurate results. The decomposition is expressed by the equation, $SnCl_2 + 2\,(NH_4O, NO_5) + 2\,HO = SnO_2 + 2\,NH_4Cl + 2\,(NO_5, HO)$, or, in precipitating with sulphate of soda: $SnCl_2 + 4\,(NaO, SO_3) + 2\,HO = SnO_2 + 2\,NaCl + 2\,(NaO, HO, 2\,SO_3)$.

Tin may also, according to H. ROSE,† be completely precipitated from solutions of the binoxide or bichloride, by sulphuric acid. If the solution contains metastannic acid or metachloride of tin, the precipitation is effected without extraordinary dilution; on the contrary, if it contains the other modification of the binoxide or bichloride, very considerable dilution is necessary. If free hydrochloric acid is absent, the precipitation is rapid; in other cases 12 or 24 hours at least are required for perfect precipitation. Allow to settle thoroughly, before filtering, wash well (if hydrochloric acid was present, till the washings give no turbidity with nitrate of silver), dry and ignite, at last intensely with addition of some carbonate of ammonia. The results obtained by OESTEN, and communicated by H. ROSE, are exact.

c. By Precipitation as Protosulphide or Bisulphide of Tin.

Precipitate the dilute moderately acid solution with sulphuretted hydrogen water or gas. If the tin was present in the solution in the form of protoxide, and the precipitate consists accordingly of the brown protosulphide, keep the solution, supersaturated with sulphuretted hydrogen, standing for half an hour in a moderately warm place, and then filter; if, on the other hand, the solution contain a salt of binoxide of tin, and the precipitate consists accordingly of the yellow bisulphide, put the fluid, loosely covered, in a warm place, until the odor of sulphuretted hydrogen has nearly gone off, and then filter. The washing of the bisulphide of tin precipitate which has a great inclination to pass through the filter, is best effected with a concentrated solution of chloride of sodium, the remains of the latter being got rid of by a solution of acetate of ammonia containing a small excess of acetic acid. If there is no objection to having the latter salt in the filtrate, the washing may be entirely effected by its means (Bunsen[*]). Put the filter, with the not yet quite dry precipitate on it, into a porcelain crucible, and apply a very gentle heat, with free access of air, until the odor of sulphurous acid is no longer perceptible. Increase the heat now gradually to a high degree of intensity, and treat the residue repeatedly with some carbonate of ammonia (see *a*), in order to insure the complete expulsion of the sulphuric acid which may be present. Were you to apply a very intense heat from the beginning, fumes of bisulphide of tin would escape, which burn to binoxide (H. Rose). For the properties of the precipitates, see § 91. The results are accurate.

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* Journ. f. prakt. Chem. 56, 366.

† Pogg. Annal. 112, 164.

2. *Volumetric Methods.*

The determination of tin by the conversion of the proto- into bichloride with the aid of oxidizing agents (bichromate of potassa, iodine, permanganate of potassa, &c.) offers peculiar difficulties, inasmuch as on the one hand the protochloride of tin takes up oxygen from the air and from the water used for dilution, with more or less rapidity, according to circumstances; and on the other hand, the energy of the oxidizing agent is not always the same, being influenced by the state of dilution and the presence of a larger or smaller excess of acid.

In the following methods, these sources of error are avoided or limited in such a manner as to render the results satisfactory.

1. *Estimation of Protochloride of Tin by Iodine in Alkaline Solution (after* Lenssen[†]).

Dissolve the protosalt of tin or the metallic tin[‡] in hydrochloric acid (preferably in a stream of carbonic acid), add Rochelle salt, then bicarbonate of soda in excess. To the clear alkaline solution thus formed add some starch-solution, and afterwards the iodine solution of § 146, till a permanent blue coloration appears. 1 eq. free iodine used corresponds to 1 eq. tin.

Lenssen's results are entirely satisfactory.

2. *Estimation of the Protochloride of Tin, after addition of Sesquichloride of Iron.*

Protochloride of tin in acid solution is best oxidized by oxidizing agents after being mixed with sesquichloride of iron (Löwenthal,[§] Stromeyer[‖]).

a. The given substance is a proto-salt of tin. Dissolve in pure sesquichloride of iron (free from protochloride) with addition of hydrochloric acid, dilute and add standard permanganate from the burette. Now make another experiment with the same quantity of water similarly colored with sesquichloride of iron to ascertain how much permanganate is required to tinge the liquid, and subtract the quantity so used from the amount employed in the actual analysis, and from the remainder calculate the tin.

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[*] Annal. d. Chem. u. Pharm. 106, 13.

[†] Journ. f. prakt. Chem. 78, 200; Annal. d. Chem. u. Pharm. 114, 113.

[‡] The solution of metallic tin is much assisted by the presence of platinum foil, which is accordingly added. Lenssen found this addition of platinum to be objectionable; but no other experimenter has observed that it interferes with the accuracy of the results.

[§] Journ. f. prakt. Chem. 76, 484. [‖] Annal. d. Chem. u. Pharm. 117, 261.

The reaction between the tin salt and the iron solution is $SnCl + Fe_2Cl_3 = SnCl_2 + 2\ Fe\ Cl$. The solution thus contains protochloride of iron in the place of proto-salt of tin, the former being, as is well known, far less susceptible of alteration from the action of free oxygen than the latter. 2 eq. iron found correspond to 1 eq. tin.

b. The given substance is metallic tin. Either dissolve in hydrochloric acid—preferably with addition of platinum and in an atmosphere of carbonic acid—and treat the solution according to *a*, or place the substance at once in a concentrated solution of sesquichloride of iron, mixed with a little hydrochloric acid; under these circumstances it will, if finely divided, dissolve quickly even in the cold and without evolution of hydrogen. Gentle warming is unobjectionable. Now add the permanganate. The reaction is $Sn + 2\ Fe_2\ Cl_3 = Sn\ Cl_2 + 4\ Fe\ Cl$, therefore every 4 eq. iron found reduced correspond to 1 eq. tin. The results are of course only correct when iron is not present. Where this is the case, proceed with the impure tin solution according to *c*.

c. The given substance is bichloride of tin, or binoxide of tin, or a compound of tin containing iron. Dissolve in water with addition of hydrochloric acid, place a plate of zinc in the solution and allow to stand twelve hours, then remove the precipitated tin with a brush, wash it, dissolve in sesquichloride of iron, and proceed as in *b*.

d. The given substance is pure bisulphide of tin, precipitated out of an acid solution of binoxide free from protoxide. Mix with sesquichloride of iron, heat gently, filter off the sulphur, and then add the permanganate. 4 eq. iron correspond to 1 eq. tin, for $SnS_2 + 2\ Fe_2Cl_3 = SnCl_2 + 4\ FeCl + 2\ S$. The results obtained by STROMEYER are quite satisfactory.

§ 127.

6. ARSENIOUS ACID, and 7. ARSENIC ACID.

a. Solution.

The compounds of arsenious and arsenic acids which are not soluble in water are dissolved in hydrochloric acid or in nitrohydrochloric acid. Some native arseniates require fusing with carbonate of soda. Metallic arsenic, sulphide of arsenic and metallic arsenides are dissolved in fuming nitric acid or nitrohydrochloric acid; those metallic arsenides which are insoluble in these menstrua are fused with carbonate of soda and nitrate of potassa, by which means they are converted into soluble arseniates of the alkalies and insoluble metallic oxides, or they may be suspended in potassa solution and treated with chlorine (§ 164, B, 7). In this last manner too, sulphide of arsenic, dissolved in concentrated potassa, may be very easily rendered soluble. All solutions of compounds of arsenic which have been effected by long heating with fuming nitric acid, or by warming with excess of nitrohydrochloric acid, or chlorine, contain arsenic acid. A solution of arsenious acid in hydrochloric acid cannot be concentrated by evaporation, since chloride of arsenic would escape with the hydrochloric acid fumes. This, however, less readily takes place if the solution contains arsenic acid; it is advisable in all cases where a hydrochloric acid solution containing arsenic is to be concentrated, previously to render the same alkaline.

b. Determination.

Arsenic is weighed as *arseniate of lead*, or as *arseniate of magnesia and ammonia*, or as *arseniate of sesquioxide of iron*, or as *tersulphide of arsenic*. The determination as arseniate of magnesia and ammonia is sometimes preceded by precipitation as arsenio-molybdate of ammonia. Arsenic may be estimated also in an *indirect* way, and by *volumetric methods.*

We may convert into

1. Arseniate of Lead.

Arsenious and arsenic acids in aqueous or nitric acid solution. (Acids or halogens forming fixed salts with oxide of lead or metallic lead, must not be present.)

2. Arseniate of Magnesia and Ammonia.

a. By Direct Precipitation.

Arsenic acid in all solutions free from bases or acids precipitable by magnesia or ammonia.

b. Preceded by Precipitation as Arsenio-Molybdate of Ammonia.

Arsenic acid in all cases where no phosphoric acid is present, nor any substance by which molybdic acid is decomposed.

3. Arseniate of Sesquioxide of Iron.

Arsenic acid in solutions free from substances precipitable by sesquichloride of iron with addition of ammonia or carbonate of baryta.

4. Tersulphide of Arsenic.

All compounds of arsenic without exception.

Arsenic may be determined volumetrically in a simple and exact manner, whether present in the form of arsenious acid or an alkaline arsenite, or as arsenic acid or an alkaline arseniate. The volumetric methods have now almost entirely superseded the indirect gravimetric methods formerly employed to effect the estimation of arsenious acid.

1. *Determination as Arseniate of Lead.*

a. Arsenic Acid in Aqueous Solution.

A weighed portion of the solution is put into a platinum or porcelain dish, and a weighed amount of recently ignited pure oxide of lead added (about five or six times the supposed quantity of arsenic acid present) the mixture is cautiously evaporated to dryness, and the residue heated to gentle redness, and maintained some time at this temperature. The residue is arseniate of lead + oxide of lead. The quantity of arsenic acid is now readily found by subtracting from the weight of the residue that of the oxide of lead added.

For the properties of arseniate of lead, see § 92. The results are perfectly accurate, provided the residue be not heated beyond gentle redness.

b. Arsenious Acid in Solution.

Mix the solution with nitric acid, evaporate to a small bulk, add a weighed quantity of oxide of lead in excess, evaporate to dryness, and ignite the residue most cautiously in a covered crucible, until the whole of the nitrate of lead is decomposed. The residue consists here also of arsenic acid + oxide of lead. This method requires considerable care to guard against loss by decrepitation upon ignition of the nitrate of lead.

2. *Estimation as Arseniate of Magnesia and Ammonia.*

a. By Direct Precipitation.

This method, which was first recommended by LEVOL, presupposes that the whole of the arsenic is contained in the solution in the form of arsenic acid. Where this is not the case, the solution is gently heated, in a capacious flask, with hydrochloric acid, and chlorate of potassa added in small portions, until the fluid emits a strong smell of chlorous acid; it is then allowed to stand at a gentle heat until the odor of this gas is nearly gone off.

The arsenic acid solution is now mixed with ammonia in excess, which must not produce turbidity, even after standing some time; a solution of sulphate of magnesia is then added, containing chloride of ammonium in sufficient quantity to prevent its being rendered turbid by ammonia. (The best way is to keep a solution of sulphate of magnesia mixed with chloride of ammonium and ammonia ready prepared in the laboratory—see § 62, 6.) The fluid, which smells strongly of ammonia, is allowed to stand 12 hours in the cold, and then filtered through a weighed filter. The precipitate is then transferred to the filter, with the aid of portions of the filtrate so as to use no more washing water than necessary, and washed with small quantities of a mixture of three parts water and one part ammonia, till the washings on being mixed with nitric acid and nitrate of silver show only a slight opalescence. The precipitate is dried at 105 to 110°, and weighed. It has the formula, $2\,Mg\,O, N\,H_4\,O, As\,O_5 + aq.$*

For its properties, see § 92. This process yields, it is true, satisfactory results, but they are still always somewhat too low, as the precipitate is perceptibly soluble even in ammoniacal water. The error may be diminished by measuring the filtrate (without the washings) and adding for every 16 c. c. 1 mgrm. to the weight found of the precipitate. To extend the correction to the washings is inadmissible, since they cannot be regarded as a saturated solution.

b. Preceded by Precipitation as Arsenio-Molybdate of Ammonia.

Mix the acid solution, which must be free from phosphoric and silicic acids, with an excess of solution of molybdate of ammonia. The molybdate of ammonia solution should have been previously mixed with nitric acid in excess, and the whole process is conducted exactly as in the case of phosphoric acid—see § 134, *b*, β. Treat the arseniate of magnesia and ammonia thrown down from the ammoniacal solution of the arsenio-molybdate of ammonia with a mixture of sulphate of magnesia and chloride of ammonium, as in *a*. Results satisfactory.

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* If it is dried in a water-bath, the drying must be extremely prolonged, or otherwise more than 1 aq. will be left. After brief drying in the water-bath the compound contains between 1 and 3 eq. water.

3. *Estimation as Arseniate of Sesquioxide of Iron.*

(BERTHIER and v. KOBELL'S method.)

a. The Solution contains no other fixed Bases besides Alkalies.

Add to the solution a measured quantity of solution of sesquioxide of iron of known strength, and precipitate with ammonia. (The precipitate must be reddish brown: if not of that color, it is a sign that a sufficient quantity of the solution of sesquioxide of iron has not been added.) Allow to stand some time at a gentle heat; filter, wash, and dry the precipitate; then expose first to a very gentle heat, to insure the expulsion of the ammonia at a temperature at which it cannot exercise a reducing action upon the arsenic acid; after a time, increase the heat gradually, at last subjecting the residue to intense ignition, till the weight remains constant. The residue is basic arseniate of sesquioxide of iron + sesquioxide of iron, or in other words, sesquioxide of iron + arsenic acid. Deduct from the weight of the residue the weight of the sesquioxide of iron added: the difference expresses the quantity of arsenic acid contained in the analyzed solution. A solution of sesquioxide of iron of known strength for the above purpose is best prepared by dissolving fine iron wire in nitric acid by the aid of heat, diluting suitably, and determining the sesquioxide of iron in 10 c. c. by precipitation with ammonia (see § 113, 1, *a*). The presence of a small amount of silicic acid in the solution of sesquioxide of iron is then without injurious influence, since the same is weighed with the iron both in the determination of the strength of the solution and in the arsenic-estimation.

b. The Solution contains other fixed Bases besides Alkalies.

The preceding method of BERTHIER is modified by v. KOBELL as follows, provided the bases present in the solution are not precipitated by carbonate of baryta in the cold. The solution is mixed with solution of sesquioxide of iron of known strength, as in *a*, but instead of ammonia, carbonate of baryta is added in excess (should the fluid contain a large excess of free acid, it is advisable to nearly neutralize this previously with carbonate of soda; the fluid must, however, still remain clear). The mixture is then allowed to stand several hours in the cold, and the precipitate, which contains the whole of the sesquioxide of iron, the whole of the arsenic acid, and the excess of carbonate of baryta, is washed with cold water, first by decantation, then upon the filter, dried, gently ignited *for some time*, and weighed. The residue is dissolved in hydrochloric acid, the amount of baryta contained in it determined by means of sulphuric acid, the sulphate of baryta obtained calculated to carbonate, and the calculated weight, together with the known weight of the sesquioxide of iron, subtracted from the weight of the original residue: the difference expresses the quantity of arsenic acid contained in the analyzed solution. This method presupposes the absence of sulphuric acid. In cases, therefore, where that acid is present, it must be removed before the carbonate of baryta can be added; which is effected by precipitating with chloride of barium, and filtering off the precipitate.

4. *Determination as Tersulphide of Arsenic.*

a. In Solutions of Arsenious Acid or Arsenites, free from Arsenic Acid.

Precipitate with sulphuretted hydrogen, and expel the excess of the precipitant by carbonic acid, conducting the process in the same way as with antimony—see § 125, 1. Wash the precipitated tersulphide of arsenic, dry at 100°, and weigh. Particles of the precipitate adhering so firmly to the glass tube that mechanical means fail to remove them are dissolved in ammonia, and then reprecipitated by hydrochloric acid. For the properties of the precipitate, see § 92. The results are accurate.

If the solution contains a substance which decomposes sulphuretted hydrogen, such as sesquioxide of iron, chromic acid, &c., the free sulphur which precipitates with the tersulphide of arsenic destroys the accuracy of the results. In such cases the precipitate is dissolved in solution of potassa, and chlorine transmitted through the solution (§ 148, II. 2, *b*). In the solution produced, which contains the sulphur as sulphuric acid, the arsenic as arsenic acid, the latter is determined as in 2, *a*; or the sulphuric acid is estimated, the quantity found calculated to sulphur, and the calculated weight of the latter subtracted from that of the mixed precipitate of tersulphide of arsenic and sulphur. No loss of arsenic by volatilization of the chloride takes place in this method of oxidizing the sulphide of arsenic, since the solution remains alkaline. The object may also be conveniently attained by the use of nitric acid. A very strong fuming acid, of 86° boiling point, is employed; an acid of 1·42 sp. gr. which boils at a higher temperature does not answer the purpose, as the separated sulphur would fuse, and its oxidation would be much retarded. The well-dried precipitate is shaken into a small porcelain dish, treated with a tolerably large excess of the fuming nitric acid, the dish immediately covered with a clock-glass, and as soon as the turbulence of the first action has somewhat abated, heated on a water-bath, till all the sulphur has disappeared, and the nitric acid has evaporated to a small volume. The filter to which the unremovable traces of sulphide of arsenic adhere is treated separately in the same manner, the complete destruction of the organic matter being finally effected by *gently* warming the somewhat dilute solution with chlorate of potassa (BUNSEN *). Or the filter may instead be extracted with ammonia, the solution evaporated in a separate dish, and the residual tersulphide treated as above. In the mixed solution the arsenic acid is finally precipitated as arseniate of magnesia and ammonia (§ 127, 2). Treatment of the impure precipitate with ammonia, whereby the sulphide is dissolved, and the sulphur is supposed to remain behind, only gives approximate results, as the ammoniacal solution of tersulphide of arsenic takes up a little sulphur. Small quantities of admixed free sulphur may be also removed without difficulty by bisulphide of carbon; but I cannot recommend this method where large quantities of sulphur are to be extracted. If the precipitate is moist, before using this solvent, the water should be got rid of by twice treating with absolute alcohol.

b. In Solutions of Arsenic Acid or Arseniates, or of a mixture of the two Oxides of Arsenic.

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* Annal. d. Chem. u. Pharm. 106, 10.

Heat the solution in a flask (preferably on an iron plate) to about 70°, and conduct sulphuretted hydrogen at the same time into the fluid, as long as precipitation take place. The precipitate formed is always a mixture of sulphur and tersulphide of arsenic, since the arsenic acid is first reduced to arsenious acid with separation of sulphur, and then the former is decomposed (H. Rose*).

Only in the case when a sulphosalt containing pentasulphide of arsenic is decomposed with an acid, is the precipitate actually pentasulphide, and not merely a mixture of sulphur with tersulphide (A. Fuchs †). Whichever may be the constitution of the precipitate, either the arsenic or the sulphur in it must be determined, after drying and weighing, by one of the methods given in 4, *a*.

5. *Volumetric Methods.*

a. Method which presupposes the presence of Arsenious Acid.

Bunsen's method.‡ If bichromate of potassa is boiled with concentrated hydrochloric acid, 3 eq. chlorine are disengaged to every 2 eq. chromic acid ($2\ Cr\ O_3+6\ H\ Cl=Cr_2\ Cl_3+3\ Cl+6\ H\ O$). But if arsenious acid is present (not in excess) there is not the quantity of chlorine disengaged corresponding to the chromic acid, but so much less of that element as is required to convert the arsenious into arsenic acid ($As\ O_3+2\ Cl+2\ H\ O=As\ O_5+2\ H\ Cl$). Consequently, for every 2 eq. chlorine wanting is to be reckoned 1 eq. arsenious acid. The quantity of chlorine is estimated as directed 130, I. *d*, β.

b. Method, which presupposes the presence of Arsenic Acid.

This method depends on the precipitation of the arsenic acid by uranium solution and the recognition of the end of the reaction by means of ferrocyanide of potassium. It is therefore the same as was suggested for phosphoric acid by Leconte, and brought into use by Neubauer, § and afterwards by Pincus. ‖

Bödeker,¶ who first employed the process for arsenic acid, recommends the employment of a solution of nitrate of sesquioxide of uranium, as this is more permanent than the hitherto used acetate, which is gradually decomposed by the action of light.

The uranium solution has the correct degree of dilution, if it contains about 20 grm. sesquioxide of uranium in 1 litre. It should contain as little free acid as possible. The determination of its value may be effected with the aid of pure arseniate of soda or by means of arsenious acid,—the latter is converted into arsenic acid by boiling with fuming nitric acid. The solution is rendered strongly alkaline with ammonia, and then distinctly acid with acetic acid. The uranium solution is now run in from the burette slowly, the liquid being well stirred all the while, till a drop of the mixture spread out on a porcelain plate, gives with a drop of ferrocyanide of potassium placed in its centre, a distinct reddish brown line where the two fluids meet. The height of the fluid in the burette is now read off, the level of the mixture in the beaker is marked with a strip of gummed paper, and the beaker is emptied and washed, filled with water with addition of about as much ammonia and acetic acid as was before employed, and the uranium solution is cautiously dropped in from the burette, till a drop taken out of the beaker and tested as above, gives an equally distinct border-line. The quantity of uranium solution used in this last experiment is the excess, which must be added to make the end-reaction plain for the dilution adopted. This amount is subtracted from that used in the first experiment, and we then know the exact value of the uranium solution with reference to arsenic acid.

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* Pogg. Annal. 107, 186.

† Zeitschrift f. anal. Chem. 1, 189.

‡ Annal. d. Chem. u. Pharm. 86, 290.

§ Archiv. für wissenschaftliche Heilkunde, Bd. iv. S. 228.

‖ Journ. f. prakt. Chem. 76, 104.

¶ Annal. d. Chem. u. Pharm. 117, 195.

In an actual analysis, the arsenic is first brought into the form of arsenic acid, a clear solution is obtained containing acetate of ammonia and some free acetic acid,* and the process is conducted exactly as in determining the value of the standard solution. The experiment to ascertain the correction must not be omitted here, otherwise errors are sure to arise from the different degrees of dilution of the arsenic acid solutions used in the determination of the value of the standard solution and in the actual analyses. The results of two determinations of arsenic given by BÖDEKER are satisfactory. To execute the method well requires practice.

6. *Estimation of Arsenious Acid by Indirect Gravimetric Analysis.*

a. ROSE's method. Add to the hydrochloric acid solution, in the preparation of which care must be taken to exclude oxidizing substances, a solution of sodio- or ammonio-terchloride of gold in excess, and digest the mixture for several days, in the cold, or, in the case of dilute solutions, at a gentle warmth; then weigh the separated gold as directed in § 123. Keep the filtrate to make quite sure that no more gold will separate. 2 eq. gold correspond to 3 eq. arsenious acid.

b. VOHL's † method. Mix the solution under examination with a weighed quantity of bichromate of potassa, and free sulphuric acid; estimate the chromic acid still present by the method given in § 130, *c*, and deduce from the quantity of that acid consumed in the process, *i. e.*, reduced by the arsenious acid, the quantity of the latter, after the formula $3\ As\ O_3 + 4\ Cr\ O_3 = 3\ As\ O_5 + 2\ Cr_2\ O_3$.

Supplement to the Sixth Group.

§ 128.

8. MOLYBDIC ACID.

Molybdic acid is converted, for the purpose of its estimation, either into binoxide of molybdenum, or into molybdate of lead, or into bisulphide of molybdenum.

a. Pure molybdic acid ($Mo\ O_3$), and also molybdate of ammonia, may be reduced to binoxide by heating in a current of hydrogen gas. This may be done either in a porcelain boat, placed in a wide glass tube, or in a platinum or porcelain crucible with perforated cover (§ 108, fig. 47, p. 181). The operation is continued till the weight remains constant. The temperature must not exceed a gentle redness, otherwise the binoxide itself might lose oxygen and become partially converted into metal.

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* Alkalies, alkaline earths and oxide of zinc may be present, but not such metals as yield colored precipitates with ferrocyanide of potassium, as, for instance, copper.

† Anal. d. Chem. u. Pharm. 94, 219.

In the case of molybdate of ammonia the heat must be very low at first on account of the frothing.

b. The following is the best method of precipitating molybdic acid from an alkaline solution. Dilute the solution, if necessary, neutralize the free alkali with nitric acid, and allow the carbonic acid, which may be liberated in the process, to escape, then add solution of neutral nitrate of suboxide of mercury. The yellow precipitate formed appears at first bulky, but after several hours' standing it shrinks; it is insoluble in the fluid, which contains an excess of nitrate of suboxide of mercury. Collect the precipitate on a filter, and wash with a dilute solution of nitrate of suboxide of mercury, as it is slightly soluble in pure water. Dry, remove the dry precipitate as completely as practicable from the filter, and determine the molybdenum in it as directed in *a* (H. ROSE); or mix the precipitate, together with the filter-ash, with a weighed quantity of ignited oxide of lead, and ignite until all the mercury is expelled; then add some nitrate of ammonia, ignite again and weigh. The excess obtained, over and above the weight of the oxide of lead used, is molybdic acid (SELIGSOHN*).

c. The precipitation of molybdenum as sulphide is always a difficult operation. If the acid solution is supersaturated with sulphuretted hydrogen, warmed, and filtered, the filtrate and washings are generally still colored. They must, accordingly, be warmed, and sulphuretted hydrogen again added, and the operation must afterwards, if necessary, be repeated until the washings appear almost colorless. The precipitation succeeds better when the sulphide of molybdenum is dissolved in a relatively large excess of sulphide of ammonium, and, after the fluid has acquired a reddish-yellow tint, precipitated with hydrochloric acid. ZENKER† advises then to boil, until the sulphuretted hydrogen is expelled, and to wash with hot water, at first slightly acidified. The brown sulphide of molybdenum is collected on a weighed filter, and the molybdenum determined in an aliquot part of it, by gentle ignition in a current of hydrogen gas, as in *a*. The brown sulphide of molybdenum changes in this process to the gray bisulphide (H. ROSE).

II. DETERMINATION OF ACIDS IN COMPOUNDS CONTAINING ONLY ONE ACID, FREE OR COMBINED;—AND SEPARATION OF ACIDS FROM BASES.

FIRST GROUP.

First Division.

ARSENIOUS ACID—ARSENIC ACID—CHROMIC ACID—(Selenious Acid, Sulphurous and Hyposulphurous Acids, Iodic Acid, Nitrous Acid).

§ 129.

1. ARSENIOUS AND ARSENIC ACIDS.

These have been already treated of among the bases (§ 127) on account of their behavior with sulphuretted hydrogen; they are merely mentioned here to indicate the place to which they properly belong. The methods of separating them from the bases will be found in Section V.

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* Journ. f. prakt. Chem. 67, 472.

† Ibid. 58, 259.

§ 130.

2. CHROMIC ACID.

1. DETERMINATION.

Chromic acid is determined either in the form of *sesquioxide of chromium*, or in that of *chromate of lead.* But it may be estimated also from the quantity of carbonic acid disengaged by its action upon oxalic acid in excess, and also by volumetric analysis. In employing the first method, it must be borne in mind that 1 eq. sesquioxide of chromium corresponds to 2 eq. chromic acid.

a. Determination as Sesquioxide of Chromium.

α. The chromic acid is reduced to the state of sesquioxide, and the amount of the latter determined (§ 106). The reduction is effected either by heating the solution with hydrochloric acid and alcohol; or by mixing hydrochloric acid with the solution, and conducting sulphuretted hydrogen into the mixture; or by adding a strong solution of sulphurous acid, and applying a gentle heat. With concentrated solutions the first method is generally resorted to, with dilute solutions one of the two latter. With respect to the first method, I have to remark that the alcohol must be expelled before the sesquioxide of chromium can be precipitated with ammonia; and with respect to the second, that the solution supersaturated with sulphuretted hydrogen must be allowed to stand in a moderately warm place, until the separated sulphur has completely subsided. The results are accurate.

β. The neutral or slightly acid (nitric acid) solution is precipitated with nitrate of suboxide of mercury, the red precipitate of chromate of suboxide of mercury filtered off, washed with a dilute solution of nitrate of suboxide of mercury, dried, ignited, and the residuary sesquioxide of chromium weighed (H. ROSE).

b. Determination as Chromate of Lead.

The solution is mixed with acetate of soda in excess, and acetic acid added until the reaction is strongly acid; the solution is then precipitated with neutral acetate of lead. The washed precipitate is either collected on a weighed filter, dried in the water-bath, and weighed; or it is gently ignited as directed § 53, and then weighed. For the properties of the precipitate, see § 93, 2. The results are accurate.

c. Determination by means of Oxalic Acid (after VOHL).

When chromic acid and oxalic acid are brought together, the former yields oxygen to the latter: sesquioxide of chromium is formed, and carbonic acid escapes ($2\ Cr\ O_3 + 3\ C_2\ O_3 = Cr_2\ O_3 + 6\ C\ O_2$). Three eq. carbonic acid (66) correspond accordingly to one eq. chromic acid (50·24). The *modus operandi* is the same as in the analysis of manganese ores (§ 215). 1 part of chromic acid requires $2\frac{1}{4}$ parts of oxalate of soda. If it is intended to determine in the residue the alkali which was combined with the chromic acid, oxalate of ammonia is used.

d. Determination by Volumetric Analysis.

α. Schwarz's method.

The principle of this very accurate method is identical with that upon which Penny's method of determining iron is based (§ 112, 2, *b*). The execution is simple: acidify the not too dilute solution of the chromate with sulphuric acid, add in excess a measured quantity of solution of protoxide of iron, the strength of which you have previously ascertained, according to the directions of § 112, 2, *a*, or *b*, or the solution of a weighed quantity of sulphate of protoxide of iron and ammonia, free from sesquioxide, and then determine in the manner directed § 112, 2, *a*, or *b*, the quantity of protoxide of iron remaining. The difference shows the amount of iron that has been converted by the chromic acid from the state of protoxide to that of sesquioxide. 1 grm. of iron corresponds to 0·5981 of chromic acid. To determine the chromic acid in chromate of lead, the latter is, after addition of the sulphate of protoxide of iron and ammonia, most thoroughly triturated with hydrochloric acid, water added, and the analysis then proceeded with.

β. Bunsen's method.*

If a chromate is boiled with an excess of fuming hydrochloric acid, there are disengaged for every 2 eq. chromic acid 3 eq. chlorine; for instance, $KO, 2\,CrO_3 + 7\,HCl = KCl + Cr_2Cl_3 + 7\,HO + 3\,Cl$. If the escaping gas is conducted into solution of iodide of potassium in excess, the 3 eq. chlorine set free 3 eq. iodine. By determining the quantity of the latter element in the manner described in § 146, we find the quantity of the chromic acid; 381 of iodine corresponding to 100·48 of chromic acid.

The analytical process is conducted as follows:—Put the weighed sample of the chromate (say ·3 to ·4 grm.) into the little flask *d*, fig. 51, (blown before the lamp, and holding only from 36 to 40 c. c.), fill the flask to two-thirds with pure fuming hydrochloric acid (free from Cl and SO_2) and connect the bulbed evolution tube *a* with the neck of the flask by means of a stout tight-closing vulcanized india-rubber tube *c*. As shown in the engraving, *a* is a bent pipette, drawn out, at the lower end, into an upturned point. A loss of chlorine need not be apprehended on adding the hydrochloric acid, as the disengagement of that gas begins only upon the application of heat. Insert the evolution tube into the neck of the retort, which is one-third filled with solution of iodide of potassium.† This retort holds about 160 c. c. The neck presents two small expansions, blown before the lamp, and intended, the lower one, to receive the liquid which is forced up during the operation, the upper one, to serve as

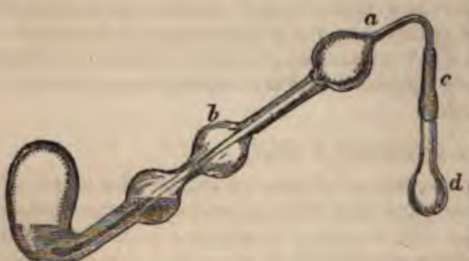

Fig. 51.

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* Annal. d. Chem. u. Pharm. 86, 279.

† 1 part of pure iodide of potassium, free from iodic acid, dissolved in 10 parts of water. The fluid must show no brown tint immediately after addition of hydrochloric acid.

additional guard against spirting. Apply heat now, cautiously, to the le flask. After two or three minutes' ebullition, the whole of the orine has passed over, and liberated its equivalent quantity of iodine in iodide of potassium solution. When the ebullition is at an end, take d of the caoutchouc tube *c* with the left hand, and, whilst steadily ding the lamp under the flask with the right, lift *a* so far out of the ort that the curved point is in the bulb *b*. Now remove first the lamp, n the flask, dip the retort in cold water, to cool it, and shake the fluid it about to effect the complete solution of the separated iodine in the ess of iodide of potassium solution. When the fluid is quite cold, nsfer it to a beaker, rinsing the retort into the beaker, and proceed as ected § 146. The method gives very satisfactory results. The appa-us here recommended differs slightly from that used by BUNSEN, the ort of the latter having only one bulbous expansion in the neck, and evolution tube no bulb, being closed instead, at the lower end, by a ss or caoutchouc valve, which permits the exit of the gas from the tube, opposes the entrance of the fluid into it. I think the modifications ich I have made in BUNSEN's apparatus are calculated to facilitate the cess of the operation.

II. SEPARATION OF CHROMIC ACID FROM THE BASES.

a. OF THE FIRST GROUP

Reduce the chromic acid as directed in I., and separate the sesqui-de of chromium from the alkalies as directed in § 155.

Mix the chromate of potassa or soda with about 2 parts of dry verized chloride of ammonium, and heat the mixture cautiously. residue contains the chlorides of the alkali metals and sesquioxide hromium, which may be separated by means of water.

Chromate of ammonia is reduced to sesquioxide of chromium by ious ignition. The ammonia is estimated in a separate portion ac-ing to § 99, 3.

b. OF THE SECOND GROUP.

Fuse the compound under examination with 4 parts of carbonate a and potassa, and treat the fused mass with hot water, which dis- the chromic acid in the form of an alkaline chromate. The resi-ntains the alkaline earths in the form of carbonates; but as they alkali, they cannot be weighed directly. The chromic acid in the is determined as in I. Chromate of baryta (and doubtless also omates of strontia and lime) may, as shown by H. ROSE,* be and completely decomposed by simple boiling with an excess of of carbonate of potassa or soda.

solve in hydrochloric acid, reduce the chromic acid according to tions of I., *a*, and separate the sesquioxide of chromium from ine earth according to § 156.

omate of magnesia as well as other chromates of the alkaline uble in water may be easily decomposed also, by determining ic acid according to I., *a*, β, or I., *b*, and separating the mag-in the filtrate from the excess of the salt of mercury or lead § 162.

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* Journ. f. prakt. Chem. 66, 166.

δ. Chromates of baryta, strontia, and lime may also be decomposed by the method described II., *a*, *β*. Compare Bahr, analysis of bichromate of baryta, lime, &c.*

c. Of the Third Group.

α. *From Alumina.*

Precipitate the alumina by ammonia or carbonate of ammonia (§ 105), and determine the chromic acid in the filtrate according to the directions given in I. (compare also § 157).

β. *From Sesquioxide of Chromium.*

aa. Determine in one portion the quantity of the chromic acid according to I., *c*, or I., *d*, *α*, or *β*, and in another portion the total amount of the chromium, by converting it all into either sesquioxide or chromic acid. The entire conversion of the substance into sesquioxide may be effected either by cautious ignition with chloride of ammonium, or according to I., *a*,—into chromic acid according to § 106, 2.

bb. In many cases the chromic acid may be precipitated according to I., *a*, *β*, or I., *b*. The sesquioxide of chromium and suboxide of mercury, or oxide of lead, in the filtrate, are separated as directed § 162.

cc. The hydrated compounds of sesquioxide of chromium with chromic acid, such as are obtained by precipitating a solution of sesquioxide of chromium with a solution of chromate of potassa, &c., may also be analyzed by ignition in a stream of dry air, the apparatus, fig. 25, p. 45, being employed. The loss of weight of the bulb-tube represents the joint amount of oxygen and water that have escaped. If the increment of the $Ca\,Cl$ tube is deducted, we shall have the oxygen. Now every 3 eq. oxygen correspond to 2 eq. of chromic acid. The amount of the latter being thus calculated, we have only to subtract its equivalent quantity of sesquioxide from the weight of residue after the ignition, and the remainder is the quantity of sesquioxide originally present. Vogel † and also Storer and Elliot ‡ have employed this method.

d. Of the Fourth Group.

α. Proceed as directed in *b*, *α*. Upon treating the fused mass with hot water, the metals are left as oxides. In the case of manganese the fusion must be effected in an atmosphere of carbonic acid gas. Apparatus, fig. 47 in § 108.

β. Reduce the chromic acid as directed in I., *a*, and separate the sesquioxide of chromium from the metals in question, as directed in § 160.

e. Of the Fifth and Sixth Groups.

α. Acidify the solution, and precipitate, either at once or after previous reduction of the chromic acid by sulphurous acid, with sulphuretted hydrogen. The metals of the fifth and sixth groups precipitate in conjunction with free sulphur (§§ 115 to 127), the chromic acid is reduced. Flter and determine the sesquioxide of chromium in the filtrate, as directed in I., *a*.

β. Chromate of lead may be conveniently decomposed by heating with hydrochloric acid and some alcohol; the chloride of lead and sesquichloride of chromium formed are subsequently separated by means of alcohol (compare § 162). The alcoholic solution ought always to be tested with sulphuric acid; should a precipitate of sulphate of lead form, this must be filtered off, weighed, and taken into account (compare also § 130, I., *d*).

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* Journ. f. prakt. Chem. 60, 60.

† Ibid. 77, 484.

‡ Proceedings of the American Academy, vol. v. p. 198.

Supplement to the First Division.

§ 131.

1. SELENIOUS ACID.

From aqueous or hydrochloric acid solutions of selenious acid, the selenium is precipitated by sulphurous acid gas or, in presence of an excess of acid, by sulphite of soda, or sulphite of ammonia. If the solution contains nitric acid, this must be removed first by evaporation with hydrochloric acid. The precipitated liquid is heated to boiling for ¼ hour, which changes the precipitate from its original red color to black, and makes it dense and heavy. The liquid is tested by a further addition of the reagent to see whether any more selenium will separate; the precipitate is finally collected on a weighed filter, dried at a temperature somewhat below 100°, and weighed. Since H. ROSE [*] has shown that the presence of hydrochloric acid is an essential condition to the complete reduction of the selenious acid, the former acid must be added, if not already present. To make quite sure that all the selenium has been removed, the filtrate is evaporated to a small volume, boiled with strong hydrochloric acid, so as to reduce any selenic acid to selenious acid, and tested once more with sulphurous acid.

As regards the separation of selenious acid from the bases, the following brief directions will suffice:—

a. If the bases are not liable to be altered by the action of sulphurous acid and hydrochloric acid, the selenium may be at once precipitated in the way just given; the filtrate, when evaporated with sulphuric acid, yields the base as sulphate.

b. From bases which are not thrown down from acid solution by hydrosulphuric acid, the selenious acid may be separated by sulphuretted hydrogen. The precipitate is, according to H. ROSE, a mixture of 1 eq. selenium with 2 eq. sulphur. If it is dried at or a little below 100°, the weight of the selenium may be accurately ascertained. Should, however, extra sulphur be mixed with the precipitate, the latter is oxidized while still moist with hydrochloric acid and chlorate of potassa, or by treatment with potassa solution with simultaneous heating and transmission of chlorine. It is necessary here to oxidize the sulphur completely, as it may inclose selenium. The solution now containing selenic acid is heated until it smells no longer of chlorine, hydrochloric acid is added, and the mixture is reheated. The selenic acid is hereby reduced to selenious acid, and when the solution has again ceased to smell of chlorine, the selenium is precipitated with sulphurous acid.

c. In many selenites or selenates the selenium may also be determined, by converting first into selenocyanide of potassium, and precipitating the aqueous solution of the latter with hydrochloric acid (OPPENHEIM [†]).

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[*] Zeitschrift f. analyt. Chem. 1, 73.

[†] Journ f. prakt. Chem. 71, 280.

To this end the substance is mixed with 7 or 8 times its quantity of ordinary cyanide of potassium (containing cyanic acid), the mixture is put into a long-necked flask, or a porcelain crucible, covered with a layer of cyanide of potassium, and fused in a stream of hydrogen. The temperature is kept so low that the glass or porcelain is not attacked, and while cooling care must be taken to exclude atmospheric air. When cold, the brown mass is treated with water, and the colorless solution filtered, if necessary. The liquid should be somewhat but not immoderately diluted. Now boil some time (in order to convert the small quantity of selenide of potassium that may be present into selenocyanide of potassium by the excess of cyanide of potassium), allow to cool, supersaturate with hydrochloric acid, and heat again for some time. At the end of 12 or 24 hours all selenium will have separated, filter, dry at 100°, and weigh. The results obtained by this process are accurate (H. Rose [*]).

If the selenium agglomerates together on heating, it may inclose salts. In such cases, by way of control, it should be redissolved in nitric acid, and, after addition of hydrochloric acid, precipitated with sulphurous acid. The fluid filtered off from the selenious precipitate is, as a rule, free from selenium; it is, however, always well to satisfy one's self on this point by the addition of sulphurous acid.

d. From many bases the selenious acid (and also the selenic acid) may be separated by fusing the compound with 2 parts of carbonate of soda and 1 part of nitrate of potassa, extracting the fused mass thoroughly by boiling with water, saturating the filtrate, if necessary, with carbonic acid, to free it from lead which it might contain, then boiling down with hydrochloric acid in excess (to reduce the selenic acid and drive off the nitric acid), and precipitating finally with sulphurous acid.

Selenium, if pure, must volatilize without residue when heated in a tube.

2. Sulphurous Acid.

To estimate free sulphurous acid in a fluid which may contain also other acids (sulphuric acid, hydrochloric acid, acetic acid), a weighed quantity of the fluid is diluted with water, absolutely free from air,[†] until the diluted liquid contains not more than 0·05 per cent. by weight of sulphurous acid; some starch-paste is now added, and then standard solution of iodide, until the iodide of starch reaction makes its appearance. The reaction, which, under these circumstances, takes place is represented by the equation

$$I+H\,O+S\,O_2=H\,I+S\,O_3 \text{ (Bunsen).}$$

1 equivalent of iodine added corresponds accordingly to 1 equivalent of sulphurous acid. For the details of the process I refer to § 146. In the case of sulphites soluble in water or acids, water perfectly free from air is poured over the substance under examination, in sufficient quantity to attain the degree of dilution stated above, sulphuric or hydrochloric acid added in excess, and then starch-paste and solution of iodine as above. The greatest care must be taken in this method, to use, for the purpose of dilution, water absolutely from air.

Sulphurous acid may also be determined in the gravimetric way, by conversion into sulphuric acid, and precipitation of the latter with baryta, according to the directions of § 132. This method is especially applicable in the case of sulphites quite free from sulphuric acid. The conversion of the sulphurous into sulphuric acid is effected in the wet way best by saturating the fluid with chlorine, and warming; in the dry way, by heating the salt, in a platinum crucible, with 4 parts of a mixture of equal parts of carbonate of soda and nitrate of potassa.

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[*] Zeitschrift f. analyt. Chem. 1, 73.

[†] Prepared by long-continued boiling and subsequent cooling with exclusio of air.

3. HYPOSULPHUROUS ACID.

Hyposulphurous acid, in form of soluble hyposulphites, may be determined by means of iodine, in a similar way to sulphurous acid. The reaction is represented by the equation

$$2\,(\mathrm{Na\,O, S_2\,O_2}) + \mathrm{I} = \mathrm{NaO,\ S_4O_5} + \mathrm{NaI}.$$

The salt under examination is dissolved in a large amount of water, starch-paste added, and then solution of iodine until the blue color makes its appearance. That this method can give correct results only in cases where no other substances acting upon iodine are present, need hardly be mentioned. In the case of dilute fluids the results do not vary, if the fluid is acidified before adding the solution of iodine, and the operation proceeded with so quickly that no time is left for the free hyposulphurous acid to decompose into sulphur and sulphurous acid (FR. MOHR *). Hyposulphurous may be converted into sulphuric acid and then determined: the process is the same as for sulphurous acid.

4. IODIC ACID.

Iodic acid may be determined by the following easy method:—distil the acid, in the free state or in combination with a base, with an excess of pure fuming hydrochloric acid, in the apparatus described in § 130, *d*, β (chromic acid), receive the disengaged chlorine in solution of iodide of potassium, and determine the separated iodine as directed in § 130, *d*, β. As 1 eq. iodic acid sets free 4 eq. chlorine, and consequently 4 eq. iodine, you have to reckon 167 of iodic acid for 508 of iodine. The decomposition of iodic acid by hydrochloric acid is represented by the equation $\mathrm{I\,O_5} + 5\,\mathrm{H\,Cl} = \mathrm{ICl} + 5\,\mathrm{H\,O} + 4\,\mathrm{Cl}$ (BUNSEN †).

5. NITROUS ACID.

Nitrous acid may be determined very satisfactorily with a solution of pure permanganate of potassa, provided the fluid be sufficiently diluted to prevent the nitrous acid, which is liberated by the addition of a stronger acid, being decomposed by water with formation of nitric acid and nitric oxide. For 1 part of anhydrous nitrous acid, at least 5000 parts of water should be present. The decomposition is represented by the following equation:—$5\,\mathrm{NO_3} + 2\,\mathrm{Mn_2\,O_7} = 5\,\mathrm{N\,O_5} + 4\,\mathrm{Mn\,O}$. If the permanganate be standardized with iron dissolved to protoxide, 4 eq. iron correspond to 1 eq. $\mathrm{NO_3}$, since both of these require 2 eq. oxygen. Nitrites are dissolved in *very slightly* acidulated water, the permanganate is added till the oxidation of the nitrous acid is nearly completed, the solution is then made strongly acid, and finally permanganate is added to light-red coloration.

To determine hyponitric acid in red fuming nitric acid, transfer a few c. c. to about 500 c. c. cold pure distilled water with stirring, and determine the nitrous acid produced. 1 eq. nitrous acid found corresponds to 2 eq. hyponitric acid, for the latter—when mixed with such a large quantity of water as is indicated above—is decomposed in accordance with the following equation:—$2\,NO_4 + 2\,HO = HO, NO_5 + HO, NO_3$ (SIG. FELDHAUS*).

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* Lehrbuch der Titrirmethode, Nachträge, S. 384.

† Annal. d. Chem. u. Pharm. 86, 285.

As regards the estimation of nitrous acid with binoxide of lead, comp. *op. cit.* p. 431; also LANG's observations, *idem*, p. 484.

Second Division of the First Group of the Acids.

SULPHURIC ACID; (Hydrofluosilicic Acid).

§ 132.

SULPHURIC ACID.

I. DETERMINATION.

Sulphuric acid is usually determined in the gravimetric way as *sulphate of baryta*. The acid may, however, be estimated also by certain volumetric methods, based upon the insolubility of this salt (and the sulphate of lead).

1. *Gravimetric Method.*

Add to the sufficiently dilute solution, if necessary, some hydrochloric acid to acid reaction, heat to near ebullition, add chloride of barium in slight excess, and proceed as directed § 101, 1, *a*. The washing is always best effected by decantation first. Should the analyzed solution contain nitric acid, some nitrate of baryta is likely to precipitate in conjunction with the sulphate; the removal of this admixture of nitrate of baryta from the precipitate requires protracted washing with hot water. It is, under all circumstances, necessary to continue the washing of the precipitate until the last washings remain perfectly clear upon testing with sulphuric acid. In cases where perfect accuracy is desirable I would recommend the following proceeding. After igniting the precipitate according to the directions of § 53, and weighing, moisten it with a few drops of hydrochloric acid, add hot water, stir with a very thin glass rod or with a platinum wire, rinse the rod or wire, and warm gently for some time. Pour the almost clear fluid on to a small filter, and test the filtrate with sulphuric acid. If this produces turbidity or a precipitate, which is a sign that the sulphate contains an admixture of another baryta salt, wash the residue again with hot water, until the washings are no longer rendered turbid by sulphuric acid. Dry now the precipitate in the crucible, together with the small filter, burn the latter on the lid, heat to redness, and weigh. If the sulphuric acid has been precipitated from a solution containing much nitric acid or much alkaline salt, the testing of the ignited precipitate is not merely to be recommended, but it is absolutely necessary, since in such cases it is by no means unlikely that the sulphate of baryta will contain 1 per cent. or more of nitrate of baryta or alkaline salt. The results are not always so exact as used to be believed. If precipitated in very acid solutions a little of the sulphate of baryta remains dissolved. If precipitated in very saline solutions, on the other hand, the results are generally too high, since it is difficult in this case to obtain a pure precipitate.

The sulphate of baryta has a great tendency to carry salts (especially nitrates and chlorides) down with it, which cannot be removed at all by washing, and are removed but imperfectly often when the ignited precipitate is treated with hydrochloric acid and water.* FR. STOLBA † recommends treatment with a solution of acetate of copper for the purification of impure sulphate of baryta, and demonstrates the accuracy of his process by numerous analyses, which were performed purposely under disadvantageous circumstances, *i.e.*, in the presence of much alkali- and baryta-salt. The solution of acetate of copper is prepared from the crystallized salt of the shops; if it contains no sulphuric acid, add 2 drops of the dilute acid. Dissolve it with addition of a little acetic acid in hot water, add a few drops of solution of chloride of barium, enough to give a slight baryta reaction, boil a short time and filter. The solution on cooling deposits crystals; the supernatant cold saturated solution is employed. The small addition of chloride of barium to the solution of copper containing a little sulphuric acid, is for the purpose of incapacitating the fluid for taking up any sulphate of baryta, by saturating it, so to speak, with that substance.

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* Zeitschrift f. analyt. Chem. 1, 426.

After the precipitation of the sulphuric acid has been effected in the usual manner in the fluid acidified with hydrochloric acid and the precipitate has been washed by decantation combined with filtration, till the filtrate ceases to give a reaction for baryta and chlorine (at least for baryta), treat the precipitate still in the beaker with 40 or 50 c. c. of the copper solution, add some water and acetic acid, and digest at a temperature near the boiling point for 10 or 15 minutes, with constant agitation. The acetic acid added should be sufficient to prevent the precipitation of basic salt during this operation. If, notwithstanding the precaution taken, basic salt is precipitated, it must be redissolved by addition of acetic acid (not hydrochloric acid). After the precipitate has been filtered off and washed with hot water, drop a few drops of hydrochloric acid on it, continue washing, lastly dry, ignite, and weigh.

[Sulphate of baryta may be purified, when its bulk is not too large, by dissolving in the crucible, after ignition, in pure concentrated and hot sulphuric acid. On diluting copiously with water, the sulphate separates and may be washed with hot water.‡]

2. *Volumetric Methods.*

a. After CARL MOHR.§ Make a standard solution by dissolving 1 eq. (*i.e.*, 121·96 grm.) pure cystallized chloride of barium ($Ba\ Cl + 2\ aq.$) to 1 litre. Add to the fluid to be examined for sulphuric acid—which, should it contain much free acid, is previously to be nearly neutralized with pure carbonate of soda—a measured quantity of this solution, best a round number of cubic centimetres, in more than sufficient proportion to precipitate the sulphuric acid, but not in too great excess. Digest the mixture for some time in a warm place, then precipitate, without previous filtration, the excess of chloride of barium with carbonate of ammonia and a little caustic ammonia, filter off the precipitate consisting of sulphate and carbonate of baryta, wash until the water running off acts no longer upon sensitive red litmus paper, and then determine the carbonate of baryta in the precipitate by the alkalimetric method given in § 210. By deducting the quantity of baryta found in the state of carbonate from that corresponding to the chloride of barium added, you find the amount of baryta equivalent to the sulphuric acid present. Suppose you have added to the fluid under examination—

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* Comp. Zeitschrift f. analyt. Chem. 1, 80.

† Ding. polyt. Journ. 168, 43; Zeitschrift f. analyt. Chem. 2, 390.

‡ [The Ed. cannot name the originator of this method, having mislaid his reference.]

§ Annal. d. Chem. u. Pharm. 90, 165.

$$\text{10 c. c. of chloride of barium solution} = 0{\cdot}765 \text{ Ba O},$$

and found, at the end of the process,

$$\text{0·300 of carbonate of baryta} = 0{\cdot}233 \quad \text{“}$$

$$\text{the remainder,} \quad 0{\cdot}532 \text{ Ba O},$$

will give you the quantity of the sulphuric acid by means of the proportion:

$$76{\cdot}5 : 40 :: 0{\cdot}532 : x;\ x = 0{\cdot}278\ (S\,O_3).$$

This calculation may be considerably simplified, by estimating the carbonate of baryta, as stated in § 210, by means of a normal solution of nitric acid; of which it consequently takes a volume equal to that of the chloride of barium solution to neutralize the carbonate of baryta precipitated from the latter, if no sulphuric acid is present; if, on the other hand, that acid is present, less of the nitric acid solution is required, the difference expressing the quantity of sulphuric acid. In the above example it took 3·04 c. c. to neutralize the carbonate of baryta formed; deducting these from the 10 c. c. used, we have left 6·96 c. c.

$$1000 : 6{\cdot}96 :: 40 : x;\ x = 0{\cdot}278\ (S\,O_3).$$

The results of this method are quite satisfactory, if the solution does not contain too much free acid; but in presence of a large excess of free acid, the action of the salt of ammonia will retain carbonate of baryta in solution, which, of course, will make the amount of sulphuric acid appear higher than is really the case. That this method is altogether inapplicable in presence of phosphoric acid, oxalic acid, or any other acid precipitating baryta salt from neutral solutions, need hardly be mentioned.

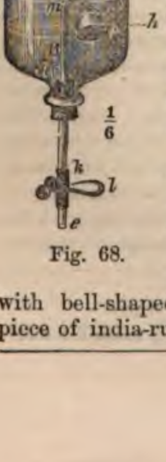

Fig. 68.

b. After R. Wildenstein (second process *). Of all the methods for the volumetric estimation of sulphuric acid, the simplest, and that which is capable of the most general application, is to drop into the solution containing excess of hydrochloric acid, standard chloride of barium solution, till the exact point is reached when no more precipitation takes place. This point is difficult to hit, and hence the method has only found a very limited use.

Wildenstein has given this method a practical form which renders it possible to complete an analysis in about half an hour, and at the same time to obtain satisfactory results. He employs the apparatus, fig. 68. *A* is bottle of white glass whose bottom has been removed it contains 900—950 c. c. *B* is a strong funnel tube with bell-shaped funnel, and bent as shown, provided below with piece of india-rubber tube, a screw compression-cock, and a small piec of tubing not drawn out. The length from *c* to *d* is about 7½-8, from *d* to *e* about 12 cm. The opening of the funnel-tube *f*, which may with advantage have a diameter of 2·5 to 3 cm. is covered as follows:—Take a piece of fine new woollen stuff or muslin, free from sulphuric acid, and about 6 cm. square, lay on it two pieces of Swedish paper of the same size, and then another piece of stuff like the first, now bind these all together over the opening *f*, carefully and without injuring the paper, by means of a strong linen thread which has been drawn a few times over wax, and cut it off even all round. We have now a small syphon-filter, which enables us to filter off a portion of fluid contained in *A*, and turbid from sulphate of baryta, clear and with comparative rapidity.

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* Zeitschrift f. analyt. Chem. 1, 432.

On gradually adding chloride of barium to the dilute acid solution of a sulphate a point occurs which may be compared to the neutral point in precipitating silver with chloride of sodium (see p. 211); *i. e.*, there is a certain moment, when a portion filtered off will give a turbidity both with sulphuric acid and chloride of barium after the lapse of a few minutes. On this account we must either proceed on the principle recommended for the estimation of silver, *i. e.*, disregarding the quantity of chloride of barium in the solution, to standardize it by adding it to a known amount of a sulphate, till a precipitate ceases to be formed; or else we must—and WILDENSTEIN recommends this latter course—consider as the end-point of the reaction the point at which chloride of barium ceases to produce a distinctly visible precipitation in the clear filtrate after a lapse of two minutes.

The chloride of barium solution is prepared by dissolving 61 grm. $BaCl + 2 aq.$ in a litre of water; 1 c. c. corresponds to ·02 sulphuric acid.

First prepare the solution of the sulphate to be analyzed (using about 3 or 4 grm.), then fill *A* with warm water, open the cock with the screw or by the aid of a glass rod, and wait till the syphon *B* is quite full of water. If the water runs down the tube *c e* without filling it entirely, close and open the cock a few times, and this inconvenience will be removed. (It is not allowable to suck at *e*, or to fill the syphon with the wash-bottle at *e*, as either proceeding would inevitably lead to injuring the filter.) Now close the cock and pour out the warm water, replace it by 400 c. c. of boiling water, add the ready-prepared solution of the sulphate, and a suitable quantity of hydrochloric acid, if necessary, and run in the chloride of barium solution, at first in rather large portions, at last in ½ c. c. Before each fresh addition of chloride of barium open the cock and allow rather more liquid to flow into a beaker than corresponds to the contents of the syphon. This quantity should be previously ascertained, and a mark indicating it made on the beaker. Now close the cock and pour the filtrate without loss back into *A*. (As the beaker is used over and over again for the same purpose it need not be rinsed out.) Now run some of the fluid into a test tube, so as to one-third fill it, add to the clear fluid 2 drops of chloride of barium from the burette and shake. If a precipitate or turbidity is produced return the portion to the main quantity. The experiment is finished when the last portion tested shows after the lapse of exactly two minutes no distinctly visible turbidity. The drops of chloride of barium used for the last testing are of course not reckoned. The slight error involved from the fact that the small quantity of fluid in the syphon is finally unacted on, is too small to be noticed. During the experiment the filter must not be injured by the stirring. In case the point has been overstepped, add 1 c. c. of dilute sulphuric acid (equivalent to the chloride of barium) to *A*, and endeavor to hit the end-point again. Here 1 c. c. will have to be subtracted from the c. c. of chloride of barium used.

The results obtained by WILDENSTEIN are of sufficient accuracy for technical purposes. Some experiments made in my own laboratory were also quite satisfactory.

II. SEPARATION OF SULPHURIC ACID FROM THE BASES.

a. FROM THOSE BASES WITH WHICH THE ACID FORMS COMPOUNDS SOLUBLE IN WATER OR IN HYDROCHLORIC ACID.

Precipitate the sulphuric acid as in I. The filtrate which contains, besides the bases originally combined with the sulphuric acid, also the excess of the chloride of barium used, is treated by the methods given in Section V. to effect the separation of the bases in question from baryta.

b. FROM THOSE BASES WITH WHICH THE ACID FORMS COMPOUNDS INSOLUBLE OR DIFFICULTLY SOLUBLE IN WATER OR IN HYDROCHLORIC ACID.

α. From Baryta, Strontia, and Lime.

Fuse the finely pulverized compound under examination in a platinum crucible, with 5 parts of mixed carbonates of soda and potassa. Put the crucible, with its contents, into a beaker, or into a platinum or porcelain dish, pour water over it, and apply heat until the alkaline sulphates and carbonates are completely dissolved; filter the hot solution from the residuary carbonates of the earths, wash the latter thoroughly with water, to which a little ammonia and carbonate of ammonia has been added, and determine according to §§ 101 to 103. If the precipitates have been well washed, it is perfectly admissible to ignite and weigh at once. Precipitate the sulphuric acid from the filtrate, as in I. Finely pulverized sulphate of lime and sulphate of strontia may be completely decomposed also by boiling with a solution of carbonate of potassa;* the same process will answer also for sulphate of baryta; but the operation is far more difficult, and complete decomposition is effected only by boiling the precipitate, after decanting the fluid repeatedly with an excess of solution of carbonated alkali (H. ROSE †). [Sulphate of lime may be dissolved in moderately dilute hydrochloric acid, and the sulphuric acid precipitated with chloride of barium.]

β. From Oxide of Lead.

The simplest way of effecting the decomposition of sulphate of lead consists in digesting it, at the common temperature, with a solution of bicarbonate of soda or potassa, filtering, washing the precipitate, determining the sulphuric acid in the filtrate, as in I., dissolving the precipitate, which contains alkali, in nitric acid or acetic acid, and determining the lead in the solution by one of the methods given in § 162.

Presence of strontia and lime necessitates no alteration in this method; but if baryta also is present, and it is accordingly necessary to ignite ‡ the mixture with carbonated alkalies (or to boil repeatedly with fresh portions of solution of the same), a small portion of lead always remains in solution in the alkaline fluid; this must be precipitated by passing carbonic acid before filtering.

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* Carbonate of soda does not answer as well.

† Journ. f. prakt. Chem. 64, 382, and 65, 316.

‡ This ignition is most safely effected in a porcelain crucible.

Supplement to the Second Division.

§ 133.

HYDROFLUOSILICIC ACID.

If you have hydrofluosilicic acid in solution, add solution of chloride of potassium, or chloride of sodium, then a volume of strong alcohol equal to the fluid present, collect the precipitated silicofluoride of potassium or sodium on a weighed filter, and wash with a mixture of equal volumes of spirit of wine and water. Dry the washed precipitate at 100°, and weigh. Mix the alcoholic filtrate with hydrochloric acid, evaporate to dryness, and treat the residue with hydrochloric acid and water. If this leaves an undissolved residue of silicic acid, this is a sign that the examined acid contained an excess of silicic acid; the weight of the residue shows the amount of the excess.

Silicofluoride of potassium has the formula $K\,Fl, Si\,Fl_2$, silicofluoride of sodium, $Na\,Fl, Si\,Fl_2$. Both compounds are anhydrous at 100°. They dissolve with difficulty in water, and are insoluble in dilute spirit of wine. The analysis of silicofluorides of metals is best effected by heating in platinum vessels, with concentrated sulphuric acid; fluoride of silicon and hydrofluoric acid volatilize, the bases are left behind in the form of sulphates, and may, in many cases, after volatilization of the excess of sulphuric acid, be weighed as such. If the metallic silicofluorides to be analyzed contain water, mix them most intimately with 6 parts of recently ignited oxide of lead (H. ROSE), cover the mixture, in a small retort, with a layer of pure oxide of lead, weigh the retort, heat cautiously until the contents begin to fuse together, remove the aqueous vapor still remaining in the vessel by suction, and weigh the retort again when cold. The diminution of weight shows the quantity of water expelled. Do not neglect testing the drops of the escaping water with litmus paper; the result is accurate only if they have no acid reaction; compare § 35, β.

Third Division of the First Group of the Acids.

PHOSPHORIC ACID—BORACIC ACID—OXALIC ACID—HYDROFLUORIC ACID.

§ 134.

1. PHOSPHORIC ACID.

I. DETERMINATION.

Tribasic phosphoric acid may be determined in a great variety of ways. The forms in which this determination may be effected have been given already in § 93, 4. The most appropriate forms for the purpose, however, are *pyrophosphate of magnesia* and *phosphate of sesquioxide of uranium*, because they are in themselves well worthy of recommendation and can be employed in almost all cases. The determination as pyrophosphate of magnesia is frequently preceded by precipitation in another way, especially as phospho-molybdate of ammonia, occasionally as phosphate of binoxide of tin. The other forms in which phosphoric acid may be determined give also, in part, very good results, but admit only of a more limited application.

With regard to meta- and pyro-phosphoric acids, I have simply to remark here that these acids cannot be determined by any of the methods given below. The best way to effect their determination is to convert them into tribasic phosphoric acid; as follows:—

α. *In the dry way.* By protracted fusion with from 4 to 6 parts of mixed carbonates of soda and potassa. This method is, however, applicable only in the case of meta- and pyro-phosphates of the alkalies, and of those meta- or pyro-phosphates of metallic oxides which are completely decomposed by fusion with alkaline carbonates; it fails, accordingly, for instance, with the salts of alkaline earths, magnesia excepted.

β. *In the wet way.* The salt is heated for some time with a strong acid, best with concentrated sulphuric acid (WEBER[*]). This method leads only to the attainment of approximate results, in the case of all salts whose bases form soluble compounds with the acid added, since in these cases the meta- or pyro-phosphoric acid is never completely liberated; but the desired result may be fully attained by the use of any acid which forms insoluble compounds with the bases present. Respecting the partial conversion in the former case, I have found that it approaches the nearer to completeness the greater the quantity of free acid added,[†] and that the ebullition must be long-continued (comp. Expt. No. 36).

It must be borne in mind that tribasic phosphoric acid changes, at a temperature still below 150°, to pyro-phosphoric acid; thus, for instance, upon evaporating common phosphate of soda with hydrochloric acid in excess, and drying the residue at 150°, we obtain $Na\,Cl + Na\,O, H\,O, P\,O_5$.

a. Determination as Phosphate of Lead.

Proceed as with arsenic acid, § 127, 1 (*i.e.*, evaporate with a weighed quantity of oxide of lead, and ignite). This method presupposes that no other acid is present in the aqueous or nitric acid solution; it has this great advantage that it gives correct results, no matter whether the phosphoric acid present is mono-, bi-, or tribasic.

b. Determination as Pyrophosphate of Magnesia.

α. *Direct determination* (suitable in all cases in which it is quite certain that the acid is present in the tribasic state, either free or combined with an alkali).

Add to the solution a clear mixture of sulphate of magnesia, chloride of ammonium, and ammonia (see § 52, 6), as long as a precipitate continues to form; should the solution not yet evolve a strong ammoniacal odor, add some more ammonia; let the mixture stand 12—24 hours, without applying heat, the glass being covered, filter, wash the crystalline precipitate with a mixture of 3 parts of water and 1 part of solution of ammonia, until the washings, after the addition of nitric acid, are no longer rendered turbid by nitrate of silver, and proceed afterwards exactly as directed in § 104, 2. The results are very accurate (Expt. No. 89). The loss sustained from the slight solubility of the basic phosphate of magnesia and ammonia is very trifling (Expt. No. 32), and may even be altogether corrected by measuring the filtrate, and adding for every 54 c. c. 0·001 grm. pyrophosphate of magnesia. For the properties of the precipitate and residue, see § 74. If the solution contains pyrophosphoric acid, the precipitate is flocculent, and dissolves in ammoniated water (WEBER).

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[*] Pogg. Annal. 73, 137.

[†] There are, however, other considerations which forbid going too far in this respect.

β. *Indirect determination*, with previous precipitation as *phosphomolybdate of ammonia*, SONNENSCHEIN.[*] (Applicable in all cases in which the phosphoric acid is present in the tribasic state, even in presence of alkaline earths, alumina, sesquioxide of iron, &c. Tartaric acid, however, and similarly acting organic substances must be absent.)

The molybdenum solution described in the "Qual. Anal.," p. 66, is employed as the precipitant. The fluid to be examined for phosphoric acid should be concentrated, it may contain free nitric acid or sulphuric acid. Hydrochloric acid and chlorides, if present, must be removed by repeated evaporation with strong nitric acid. Transfer it to a beaker and add a considerable quantity of the molybdenum solution,—about 40 parts molybdic acid must be added for every 1 part phosphoric acid,—stir, without touching the sides, and keep covered 12 or 24 hours in a warm place (not hotter than 40°). Then remove a portion of the clear supernatant fluid with a pipette, mix it with an equal volume of molybdenum solution, and allow it to stand some time at 40°. If a further precipitation takes place, return the portion to the main quantity, add more molybdenum solution, allow to stand again 12 to 24 hours and test again.[†] When complete precipitation has been effected, transfer the precipitate to a small filter, remove the rest from the beaker by means of portions of the filtrate, and wash the precipitate with a mixture of 100 parts of molybdenum solution, 20 of nitric acid, sp. gr. 1·2, and 80 of water, which should be dropped on in small quantities. Then dissolve the precipitate in ammonia on the filter, wash the latter, neutralize a portion of the ammonia in the filtrate with hydrochloric acid (the solution must of course still remain strongly ammoniacal and clear), and precipitate with magnesia mixture (compare *a*). The results are accurate.

As this method requires so large a quantity of molybdic acid, it is usually resorted to only in cases where methods *b*, *a*, and *c* are inapplicable; and the amount of phosphoric acid in the quantity of substance taken to operate upon is not allowed to exceed 0·1 grm. Arsenic acid and silicic acid,[‡] if present, must first be removed. Of all the methods for determining phosphoric acid in the presence of sesquioxide of iron and alumina, this is the best.

γ. *Indirect determination*, with previous precipitation as *phosphate of binoxide of tin*.

After GIRARD.[§] Dissolve the substance in which the phosphoric acid is to be estimated in highly concentrated nitric acid, remove all chlorine, either by precipitation with nitrate of silver, or by repeated evaporation with nitric acid, add at least eight times as much tinfoil as there is phosphoric acid present, and warm the mixture for five or six hours, until the precipitate has completely subsided, leaving the supernatant fluid clear. Wash with hot water by decantation 8 to 10 times, and finally by filtration.

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[*] Journ. f. prakt Chem. 53, 343.

[†] [If the molybdic solution contain, as it should, 5 per cent. of molybdic acid, the addition of 12 c. c. for every centigramme of phosphoric acid (60 parts of molybdic to 1 part of phosphoric acid) will insure complete precipitation.]

[‡] Silicic acid may also be thrown down, in form of a yellow precipitate, by acid solution of molybdate of ammonia, especially in presence of much chloride of ammonium (W. Knop, Chem. Centralb. 1857, 691). Mr. Grundmann, who repeated Knop's experiments in my laboratory, obtained the same results. The precipitate dissolves in ammonia. If the solution, after addition of some chloride of ammonium, is allowed to stand for some time, the silicic acid separates, and the phosphoric acid may then be precipitated from the filtrate with magnesia-mixture; it is, however, always the safer way to remove silicic acid first.

[§] [This is a modification of the method of Reissig (Ann. Chem. u. Ph. 98, 339) founded upon that of Reynoso (Journ. f. prakt. Chem. 54, 261). The observations of Baeber (Fres. Zeit. iv., 122) have been regarded.]

The precipitate, consisting of metastannic acid and phosphate of binoxide of tin, together with a little phosphate of sesquioxide of iron and of alumina, is heated with sulphide of ammonium in excess, digested about two hours, and then filtered; the precipitate, consisting of sulphide of iron and hydrate of alumina, is washed with water to which a little sulphide of ammonium has been added, dissolved in nitric acid, and the solution thus formed mixed with the filtrate from the tin precipitate which contains the principal quantity of the bases. From the sulphide of ammonium filtrate, which contains bisulphide of tin and phosphate of ammonia, the phosphoric acid is at once precipitated by magnesia-mixture. I may add that GIRARD considers 4 to 5 parts tin sufficient for 1 part phosphoric acid. The results afforded by his test analyses are unexceptionable.

c. *Determination as Phosphate of Sesquioxide of Uranium.*

After LECONTE, A. ARENDT, and W. KNOP * (very suitable in presence of alkalies and alkaline earths, but not in presence of any notable amount of alumina; in presence of sesquioxide of iron, the method can be applied only with certain modifications, see § 135, g, γ). Where it is possible, prepare an acetic acid solution of the salt. If you have a nitric or hydrochloric acid solution, remove the greater portion of the free acid by evaporation, add ammonia until red litmus paper dipped into it turns very distinctly blue, and then redissolve the precipitate formed in acetic acid. If mineral acids were present, add also some acetate of ammonia. Mix the fluid now with solution of acetate of sesquioxide of uranium, and heat the mixture to boiling, which will cause the phosphoric acid to separate, in form of yellow phosphate of sesquioxide of uranium and ammonia.

Wash the precipitate, first by decantation, boiling up each time, then by filtration; the operation may be materially facilitated by adding, immediately after precipitation, as soon as the liquid has cooled a little, 2 or 3 drops of chloroform, and giving the mixture a vigorous shake, or boiling it once or twice. Dry the precipitate, and ignite as directed § 53. It is advisable to evaporate small quantities of nitric acid on the ignited precipitate repeatedly, and to re-ignite. The residue must have the color of the yolk of an egg. For the properties of the precipitate and residue, see § 93, 4, *e*. Should it be necessary to dissolve the ignited residue again, for the purpose of reprecipitating it, this can be done only after fusing it with a large excess of mixed carbonates of soda and potassa, and thereby converting the pyrophosphoric into tribasic phosphoric acid. Results accurate; compare the proofs given by the authors, and Expt. No. 90.

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* Leconte was the first to recommend the method of precipitating phosphoric acid from acetic acid solutions by means of a salt of uranium (Jahresb. von Liebig und Kopp, für 1853, 642); A. Arendt and W. Knop have subsequently subjected it to a careful and searching examination (Chem. Centralbl. 1856, 769, 803; and 1857, 177).

d. Determination as Basic Phosphate of Sesquioxide of Iron.

α. Proceed exactly as in the determination of arsenic acid, by v. KOBELL's modification of BERTHIER's method (§ 127, 3, *b*). The results are accurate.

β. Mix the acid fluid containing the phosphoric acid with an excess of solution of sesquichloride of iron of known strength, or with a weighed quantity of ammonia iron-alum, add, if necessary, sufficient alkali to neutralize the greater portion of the free acid, mix with acetate of soda in excess, and boil. If the quantity of solution of sesquichloride of iron added was sufficient, the precipitate must be brownish-red. This precipitate consists of basic phosphate and basic acetate of sesquioxide of iron, and contains the whole of the phosphoric acid and of the sesquioxide of iron. Filter off boiling, wash with boiling water mixed with some acetate of ammonia, dry carefully, and ignite in a platinum crucible with access of air (§ 53). Moisten the residue left upon ignition with strong nitric acid, evaporate this at a gentle heat, and ignite again. Should this operation have increased the weight, which, however, is not usually the case, it must be repeated, until the weight remains constant. Deduct from the weight of the residue that of the sesquioxide of iron contained in the solution added; the difference is the phosphoric acid.

γ. (J. WEEREN's method, suitable for the estimation of the phosphoric acid in phosphates of the alkalies and alkaline earths.*) Mix the nitric acid solution of the phosphate under examination, which must contain no other strong acid, with a solution of nitrate of sesquioxide of iron of known strength, in sufficient proportion to insure the formation of a basic salt; evaporate the mixture to dryness, heat the residue to 160°, until no more nitric acid fumes escape, treat with hot water until all nitrates of the alkalies and alkaline earths are removed,† collect the yellow-ochreous precipitate on a filter, dry, ignite (see § 53), weigh, and deduct from the weight the quantity of sesquioxide of iron added.

e. Determination as Basic Phosphate of Magnesia ($3\,MgO, PO_5$).

(FR. SCHULZE's method, suitable more particularly to effect the separation of phosphoric acid from alkalies.‡)

Mix the solution of the alkaline phosphate, which contains chloride of ammonium, with a weighed excess of pure magnesia, evaporate to dryness, ignite the residue until the chloride of ammonium is expelled, and separate the magnesia, which is still present in form of chloride of magnesium, by ignition with oxide of mercury. Treat the ignited residue with water, filter the solution of the chlorides of the alkali metals, wash the precipitate, dry, ignite, and weigh. The excess of weight over that of the magnesia used shows the quantity of the phosphoric acid. Results satisfactory.

f. Determination by Volumetric Analysis.

1. *With Uranium Solution.*

The employment of this solution was recommended twelve years ago by LECONTE.§ NEUBAUER ‖ improved the method and described it in detail, and afterwards it was recommended again by PINCUS,* and subsequently by BÖDEKER.† The *principle* of the method is as follows: acetate of sesquioxide of uranium precipitates from solutions rendered acid by acetic acid, phosphate of sesquioxide of uranium, or—in the presence of considerable quantities of ammoniacal salts—phosphate of sesquioxide of uranium and ammonia. The proportion between the uranium and the phosphoric acid is the same in both compounds. Both compounds when freshly precipitated and suspended in water are left unchanged by ferrocyanide of potassium; acetate of sesquioxide of uranium, on the other hand, is indicated by this reagent with great delicacy, insoluble reddish-brown ferrocyanide of uranium being precipitated.

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* Journ. f. prakt. Chem. 67, 8.

† In presence of magnesia, warming with a solution of nitrate of ammonia is advisable.

‡ Journ. f. prakt. Chem. 63, 440.

§ Jahresber. von Liebig u. Kopp, für 1853, 642.

‖ Archiv für wissenschaftliche Heilkunde, iv. 228.

According to NEUBAUER ‡ the following *solutions* are employed:—

a. A Solution of Phosphoric Acid of known strength.

Prepared by dissolving 10·085 grm. pure, crystallized, uneffloresced, powdered, and pressed phosphate of soda in water to 1 litre. 50 c. c. contain 0·1 grm. PO_5.

b. An Acid Solution of Acetate of Soda.

Prepared by dissolving 100 grm. acetate of soda in 900 water, and adding ordinary acetic acid to 1 litre.

c. A Solution of Acetate of Sesquioxide of Uranium (§ 63, 3) in water.

This is standardized by means of the phosphate of soda solution. 1 c.c. *indicates* ·005 grm. $P\,O_5$. The solution is made at first a little stronger than necessary, so that it may contain in the litre say 22 grm. $Ur_2\,O_3$ (corresponding to 32·5 grm. $Ur_2\,O_3, \bar{A} + 2$ aq. or 34 grm. $Ur_2\,O_3, \bar{A} + 3$ aq.), its value is determined, and it is diluted accordingly. To determine its value proceed as follows: transfer 50 c. c. of the *a* solution to a beaker, add 5 c. c. of the *b* solution, and heat in a water-bath to 90—100°. Now run in uranium solution, at first a large quantity, at last in ½ c. c., testing after each addition whether the precipitation is finished or not. For this purpose spread out one or two drops of the mixture on a white porcelain surface and introduce into the middle, by means of a thin glass rod, a small drop of ferrocyanide of potassium solution. As soon as a trace of excess of acetate of uranium is present, a reddish-brown spot forms in the drop, which, surrounded as it is by the colorless or almost colorless fluid, may be very distinctly perceived. When the final reaction has just appeared, heat a few minutes in the water-bath and repeat the testing on the porcelain. If now the reaction is still plain the experiment is concluded. If the uranium solution had been exactly of the required strength, 20 c. c. would have been used; but it is actually too concentrated, hence less than 20 c. c. must have been used. Suppose it was 18 c. c., then the solution will be right, if for every 18 c. c. we add 2 c. c. of water. If in this first experiment we find that the solution is much too strong, the solution is diluted with somewhat less water than is properly speaking required, another experiment is made, and it is then diluted exactly.

The *actual analysis* must be made under as nearly as possible similar circumstances to those under which the standardizing of the uranium solution was performed, especially as regards the acetate of soda. This salt retards the precipitation of uranium by ferrocyanide of potassium, hence

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[*] Journ. f. prakt. Chem. 76, 104.

[†] Annal. d. Chem. u. Pharm. 117, 195.

[‡] Anleitung zur Harnanalyse, 4 Aufl. S. 148.

the test drop on the porcelain plate becomes darker and darker. The analyst should accustom himself to observing the first appearance of the slightest brownish coloration in the middle of the drop, and should take this as the end-reaction. It need hardly be added that the same person must make the analysis who has standardized the solution (NEUBAUER).

The method is applicable to solutions of free phosphoric acid, and to alkaline and alkaline earthy phosphates, but cannot be employed in presence of sesquioxide of iron and alumina. Dissolve the substance in water or the least possible quantity of acetic acid, add 5 c. c. of *b* solution, dilute to 50 c. c., proceed with the addition of uranium as above, and count ·005 grm. PO_5 for every c. c. used. The results are satisfactory.

II. SEPARATION OF PHOSPHORIC ACID FROM THE BASES.

§ 135.

a. From the Alkalies (see also *d*, *h*, *k*).

α. Add chloride of ammonium, then acetate of lead, exactly, till no more precipitate is produced, filter off the precipitate consisting of phosphate and chloride of lead, wash, precipitate from the filtrate the slight excess of lead by sulphuretted hydrogen, filter and evaporate with hydrochloric acid (except in the case of lithia, when sulphuric acid is substituted for the hydrochloric acid). If the phosphoric acid is to be estimated in the same portion, proceed with the first precipitate (after washing to remove the larger quantity of chloride), according to *b*.

β. (Only applicable in the case of fixed alkalies.) Separate the phosphoric acid as phosphate of sesquioxide of iron, according to one of the methods given § 134, *d*, or as basic phosphate of magnesia, according to § 134, *e*. The alkalies are contained in the filtrate as nitrates or metallic chlorides.

b. From Baryta, Strontia, Lime, and Oxide of Lead.

The compound under examination is dissolved in hydrochloric or nitric acid, and the solution precipitated with sulphuric acid in slight excess. In the separation of phosphoric acid from strontia, lime, and oxide of lead, alcohol is added with the sulphuric acid. The phosphoric acid in the filtrate is determined according to § 134, *b*, α (after removal of the alcohol by evaporation). The determination of the phosphoric acid is effected most accurately by saturating the fluid with carbonate of soda, evaporating to dryness, and fusing the residue with the carbonates of soda and potassa. The fused mass is then dissolved in water, and the further process conducted as in § 134, *b*, α.

c. From Magnesia (see also *d*, *h*, *k*).

The phosphoric acid is separated as in § 134, *d*, α; and the magnesia and baryta in the filtrate are separated in the manner described § 154.

d. From the whole of the Alkaline Earths and fixed Alkalies (comp. *h*, *k*).

α. Dissolve in the least possible quantity of nitric acid, add a little chloride of ammonium, precipitate exactly with basic acetate of lead, precipitate the excess of lead rapidly from the filtrate by means of a little sulphuretted hydrogen, filter and determine the bases in the filtrate. Results good.

β. Dissolve in water, and—in the case of alkaline earthy phosphates

—the least possible nitric acid, add neutral nitrate of silver and then carbonate of silver, till the fluid reacts neutral. All phosphoric acid now separates as $3\,Ag\,O, P\,O_5$. Warming is unnecessary. Filter, wash the precipitate, dissolve it in dilute nitric acid, precipitate the silver with hydrochloric acid, and determine the phosphoric acid in the filtrate according to § 134 *b*, α. The filtrate from the phosphate of silver is freed from silver by hydrochloric acid, and the bases are then determined according to the methods already given (G. CHANCEL[*]). A good and convenient method. (If the substance contains alumina or sesquioxide of iron, these bases are completely precipitated by the carbonate of silver, and are found mixed with the phosphate of silver.)

γ. Separate the phosphoric acid as phosphate of sesquioxide of uranium (§ 134, *c*), and the excess of sesquioxide of uranium from the alkaline earths, &c., in the filtrate, according to § 161, Supplement. Results good.

δ. Separate the phosphoric acid according to § 134, *d*, β or γ. The alkaline earths are obtained in solution, in the first case, as metallic chlorides together with alkaline acetate and alkaline metallic chloride; in the second case as nitrates. Results good.

e. From Alumina (see also *h* and *k*).

α. (OTTO and FRESENIUS, applicable in presence of sesquioxide of iron.) Dissolve in hydrochloric or nitric acid, dilute a little, add a tolerable quantity of tartaric acid, and then ammonia in excess. If you have added sufficient tartaric acid, the fluid must now appear clear. Add magnesia-mixture in slight excess, and allow to stand at rest for 24 hours in a covered vessel without warming, then filter, and wash the precipitate with dilute solution of ammonia; to free it completely from alumina, sesquioxide of iron, and basic tartrate of magnesia, redissolve it in hydrochloric acid, add a very little tartaric acid, and reprecipitate with ammonia. Treat the precipitate now as directed in § 134, *b*, α. To obtain the alumina contained in the filtrate, add some nitrate of potassa and a sufficient quantity of carbonate of soda to effect the decomposition of the chloride of ammonium,[†] evaporate to dryness, and ignite the residue in a platinum vessel. Dissolve in nitric or hydrochloric acid by continued application of heat, and separate the alumina from the magnesia as directed in § 156. This method is only to be recommended when the quantity of the alumina, of the sesquioxide of iron, and of the free acid is not too large, since [phosphate of magnesia and ammonia is considerably soluble in solutions of sesquisalts of iron[‡] and alumina.[§]].

β. (WACKENRODER and FRESENIUS.) Precipitate the not too acid solution with ammonia, taking care not to use a great excess of that reagent, and add chloride of barium as long as a precipitate continues to form. Digest for some time, and then filter. The precipitate contains the whole of the alumina and the whole of the phosphoric acid; the latter combined partly with alumina, partly with baryta. Filter it off, wash it a little, and dissolve in the least possible quantity of hydrochloric acid. Warm, saturate the solution with carbonate of baryta, add pure hydrate of potassa in excess, apply heat, precipitate the baryta which the solution may contain with carbonate of soda, and filter. You have now the whole of the alumina in the solution, the whole of the phosphoric acid in the precipitate. Acidify the solution with hydrochloric acid, boil with some chlorate of potassa, and precipitate as directed § 105. Dissolve the precipitate in hydrochloric acid, precipitate the baryta with dilute sulphuric acid, filter, and determine the phosphoric acid in the filtrate by precipitation with solution of magnesia in the manner described in § 134, *b*, *α*. (HERMANN has applied a perfectly similar method in his analysis of [impure] gibbsite.)

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[*] Compt. rend. 49, 997.

[†] The ignition of alumina in presence of chloride of ammonium would entail loss by the escape of chloride of aluminium (H. Rose).

[[‡] Dick, Memoirs of Geological Surveys of Great Britain, 1, 54.]

[[§] Knapp, Fres. Zeitschrift, iv., 151.]

f. From Sesquioxide of Chromium (see also *h*, *k*).

Fuse with carbonate and nitrate of soda, and separate the chromic acid and phosphoric acid in the manner described § 166.

g. From the Metallic Oxides of the Fourth Group (see also *h*, *k*).

α. Fuse with carbonate of soda. Keep in fusion for some time, and then boil the fused mass with water. Filter and wash the undissolved residue. The filtrate contains the phosphoric acid combined with soda; determine the acid as directed in § 134, *b*, *α*. Dissolve the residue, which generally retains alkali, in acid, and determine the metal by the appropriate method.

Should a small portion of manganic acid have got into the solution, this is removed by a little sulphuretted hydrogen water.

β. Dissolve in hydrochloric acid, add tartaric acid, chloride of ammonium, and ammonia, and finally, in a flask which is to be closed afterwards, sulphide of ammonium, put the flask in a moderately warm place, allowing the mixture to deposit until the fluid appears of a yellow color, without the least tint of green; filter, and determine the metals as directed in §§ 108 to 114. The phosphoric acid is found from the loss, or determined according to § 134, *b*, *α*. The magnesia-mixture may immediately be added to the filtrate, which contains sulphide of ammonium. The washed precipitate is once more dissolved, and the solution reprecipitated as in *e*, *α*. This method is not well adapted for the analysis of the phosphate of nickel.

γ. (Special method for effecting the separation of phosphoric acid from the oxides of iron. R. ARENDT and W. KNOP[*]). Dissolve in hydrochloric acid to the least possible volume of fluid, add to the clear solution protochloride of uranium[†], until the color inclines distinctly to green, and a drop of sulphocyanide of potassium no longer produces a red tint in the fluid. Add now ammonia to distinct alkaline reaction, then acetate of sesquioxide of uranium, and free acetic acid, together with a few drops of solution of acetate of protoxide of uranium,[‡] and heat to boiling. The color of the mixture must appear distinctly greenish, and not dirty. Let the solid particles *completely* subside, and then decant on to a filter; boil the precipitate with water and some chloride of ammonium, and decant again. Repeat this operation once more, and then treat the precipitate as directed in § 134, *c*. Separate the uranium and iron in the filtrate as directed § 161, Supplement. The results are satisfactory. The addition of the protochloride of uranium has for its object the reduction of the sesquichloride of iron to protochloride.

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[*] Chem. Centralbl. 1857, 182.

[†] *Preparation of the Protochloride of Uranium.*—Dissolve carbonate of sesquioxide of uranium and ammonia in double the quantity of hydrochloric acid required to effect solution, add a few drops of solution of bichloride of platinum, and throw into the mixture an excess of fine copper turnings. Heat, and let the mixture boil from 10 to 15 minutes. The fluid speedily acquires a green color, and the conversion of chloride to subchloride is soon effected. To separate the dissolved subchloride of copper, let the mixture boil until water produces a copious precipitate in a sample of it. When this point is attained, dilute the entire solution, allow it to cool, filter off the subchloride of copper, transmit through the filtrate sulphuretted hydrogen in excess; filter off the precipitated subsulphide of copper, mix the solution with chloride of ammonium, and boil until all sulphuretted hydrogen has escaped. R. Arendt and W. Knop, Chem. Centralbl., 1857, 164.

[‡] *Preparation of Acetate of Protoxide of Uranium.*—Precipitate solution of

δ. (Special method for effecting the separation of phosphoric acid from the oxides of iron, FRESENIUS.) Reduce the sesquioxide of iron in the solution, if necessary, with sulphite of soda, add pure hydrate of potassa in excess, boil until the precipitate has become black and granular, filter, and wash with boiling water. The precipitate on the filter is protosesquioxide of iron, free from phosphoric acid. The phosphoric acid in the filtrate is determined as directed in § 134, *b*, *α*.

h. From Metallic Oxides of the Second, Third, and Fourth Groups.

More especially from the alkaline earths, alumina, the protoxides of manganese, nickel, and cobalt, and oxide of zinc; also from sesquioxide of iron, if the quantity of the latter is not too considerable.

The phosphoric acid is precipitated as phosphate of binoxide of tin, according to the directions of § 134, *b*, *γ*. The filtrate contains the bases free from any foreign body requiring removal, which, of course, greatly facilitates their estimation.

i. From the Metals of the Fifth and Sixth Groups.

Dissolve in hydrochloric or nitric acid, precipitate with sulphuretted hydrogen, filter, determine the bases by the methods given in §§ 115 to 127, and the phosphoric acid in the filtrate by the method described § 134, *b*, *α*. From oxide of silver the phosphoric acid is separated in a more simple way still, by adding hydrochloric acid to the nitric acid solution; from oxide of lead it is separated most readily by the method described in *b*.

k. From all Bases without exception.

Apply SONNENSCHEIN's method (§ 134, *b*, *β*), and in the filtrate from the phospho-molybdate of ammonia separate the bases from the molybdic acid. As molybdic acid comports itself with sulphuretted hydrogen and sulphide of ammonium like a metal of the sixth group, it is best to precipitate metals of the sixth and also of the fifth group from acid solution with sulphuretted hydrogen, before proceeding to precipitate the phosphoric acid with molybdic acid; the latter will then have to be separated only from the metals of the first four groups. This is done in the following manner: mix the acid fluid, in a flask, with ammonia till it acquires an alkaline reaction, add sulphide of ammonium in sufficient excess, close the mouth of the flask, and digest the mixture. As soon as the solution appears of a reddish-yellow color, without the least tint of green, filter off the fluid, which contains sulphide of molybdenum and ammonium, wash the residue with water mixed with some sulphide of ammonium, and separate the remaining metallic sulphides and hydrated oxides of the fourth and third groups by the methods which will be found in Section V. Mix the filtrate cautiously with hydrochloric acid in mode-

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protochloride of uranium with ammonia, and dissolve the precipitate in acetic acid, best at a high temperature.

rate excess, remove the sulphide of molybdenum according to the directions of § 128, *c*, and determine the alkaline earths and alkalies in the filtrate.

This method of separating the phosphoric acid from the bases is highly to be recommended; especially in cases where a small quantity of phosphoric acid has to be determined in presence of a very large quantity of sesquioxide of iron and alumina, as, for example, in iron ores, soils, &c. As arsenic acid and silicic acid give, with molybdic acid and ammonia, similar yellow precipitates, it is necessary, if these acids are present, to remove them first. However, even if a little silico-molybdate of ammonia is mixed with the phospho-molybdate, the estimation of the phosphoric acid may yet be accurately effected (comp. § 134, *b*, β).

As the separation of the bases from the large excess of molybdic acid used is somewhat tedious, the best way is to arrange matters so that this process may be altogether dispensed with. Supposing, for instance, you have a fluid containing sesquioxide of iron, alumina, and phosphoric acid, estimate, in one portion, by cautious precipitation with ammonia, the total amount of the three bodies; in another portion the phosphoric acid, by means of molybdic acid; and in a third, the sesquioxide of iron, in the volumetric way. The difference gives the alumina.

§ 136.

2. Boracic Acid.

I. *Determination.*

The determination of the boracic acid in an aqueous or alcoholic solution cannot be effected by simply evaporating the fluid and weighing the residue, as a notable portion of the acid volatilizes and is carried off with the aqueous or alcoholic vapor. This is the case also when the solution is evaporated with oxide of lead in excess.

Boracic acid is estimated either *indirectly* or in form of *borofluoride of potassium.*

1. *Indirect Determination.*

a. Mix the solution of the boracic acid with a weighed quantity of pure carbonate of soda,[*] in amount about 1½ times the supposed quantity of the boracic acid present. Evaporate the mixture to dryness, heat the residue to fusion and weigh. The residue contains a known amount of soda, and unknown quantities of carbonic acid and boracic acid. Determine the carbonic acid by one of the methods given in § 139, and find the boracic acid from the difference (H. Rose).

b. In the method *a*, if between 1 and 2 eq. carbonate of soda are used to 1 eq. boracic acid—and this can easily be done if one knows approximately the amount of the latter present—all the carbonic acid is expelled by the boracic acid. Hence we have only to deduct the NaO from the residue to find the BO_3. As the tumultuous escape of carbonic acid may lead to loss, it is well, after having thoroughly dried the residual saline mass, to project it in small portions cautiously into the red hot crucible. Results good (F. G. Schaffgotsch [†]).

c. If a solution contains alkalies besides boracic acid, the latter may be determined, according to C. Marignac,[‡] in the following manner:—Neutralize the solution with hydrochloric acid, add double chloride of magnesium and ammonium in such quantity that 1 part of boracic acid may have at least 2 parts of magnesia, then add ammonia and evaporate to dryness. If a precipitate is formed on adding the ammonia which does not redissolve readily on warming, add more chloride of ammonium. The evaporation is conducted, at least towards the end, in a platinum dish, a few drops of ammonia being added from time to time. Ignite the dry mass, treat with boiling water, collect the insoluble precipitate (consisting of borate of magnesia mixed with excess of magnesia) on a filter, and wash with boiling water till the washings remain clear with nitrate of silver. The filtrate and washings are mixed with ammonia, evaporated to dryness, ignited, and washed with boiling water as before.

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[*] Fused carbonate of soda answers the purpose best.

[†] Pogg. Ann. 107, 427.

[‡] Zeitschrift f. analyt. Chem. 1, 405.

The two insoluble residues are ignited together in the platinum dish before used, as strongly as possible, and for a sufficiently long time, in order to decompose the slight traces of chloride of magnesium that might still be present. After weighing determine the magnesia and find the boracic acid from the difference. The estimation of the magnesia may be made by dissolving the residue in hydrochloric acid and precipitating as phosphate of magnesia and ammonia, or more quickly, and almost as accurately, by dissolving in a known quantity of standard sulphuric acid at a boiling temperature and determining the excess of acid with standard soda (comp. Alkalimetry).

Should a little platinum remain behind on dissolving the residue, it must be weighed and subtracted from the weight of the whole (unless the dish was weighed first). Results satisfactory. MARIGNAC obtained in two experiments 0·276 instead of 0·280.

2. If boracic acid is to be determined as *borofluoride of potassium*, alkalies only (preferably only potash) may be present. The process is conducted as follows:—Mix the fluid with pure solution of potassa, adding for each eq. boracic acid supposed to be present, at least 1 eq. potassa; add pure hydrofluoric acid (free from silicic acid) in excess, and evaporate, in a platinum dish, on the water-bath, to dryness. The fumes from the evaporating fluid should redden litmus paper, otherwise there is a deficiency of hydrofluoric acid. The residue consists now of $K\,Fl$, $B\,Fl_3$ and $K\,Fl, H\,Fl$. Treat the dry saline mass, at the common temperature, with a solution of 1 part of acetate of potassa in 4 parts of water, let it stand a few hours, with frequent stirring, then decant the fluid portion on to a weighed filter, and wash the precipitate repeatedly in the same way, finally on the filter, with solution of acetate of potassa, until the last rinsings are no longer precipitated by chloride of calcium. By this course of proceeding the hydrofluate of fluoride of potassium is removed, without a particle of the borofluoride of potassium being dissolved. To remove the acetate of potassa, wash the precipitate now with spirit of wine of 0·85 sp. gr., dry at 100° and weigh. As chloride of potassium, nitrate and phosphate of potassa, salts of soda, and even, though with some difficulty, sulphate of potassa, dissolve in solution of acetate of potassa, the presence of these salts does not interfere with the estimation of the boracic acid; however, salts of soda must not be present in considerable proportion, as fluoride of sodium dissolves with very great difficulty. The results obtained by this method are satisfactory. STROMEYER's experiments gave from 97·5 to 100·7, instead of 100. For the composition and properties of borofluoride of potassium, see § 93, 5. As the salt is very likely to contain silicofluoride of potassium it is indispensable to test it for that sub-

stance; this is done by placing a small sample of it on moist blue litmus paper, and putting another sample into cold concentrated sulphuric acid. If the blue paper turns red, and effervescence ensues in the sulphuric acid, the salt is impure, and contains silicofluoride of potassium. To remove this impurity, dissolve the remainder of the salt, after weighing it, in boiling water, add ammonia, and evaporate, redissolve in boiling water, add ammonia, &c., repeating the same operation at least six times. Finally, after warming once more with ammonia, filter off the silicic acid, evaporate to dryness, and treat again with solution of acetate of potassa and alcohol (A. STROMEYER*). I was obliged to modify STROMEYER's method for effecting the separation of the silicic acid, the results of my experiments having convinced me that treating the salt only once with ammonia, as recommended by that chemist, is not sufficient to effect the object in view.

II. *Separation of Boracic Acid from the Bases.*

a. From the Alkalies.

Dissolve a weighed quantity of the borate in water, add an excess of hydrochloric acid, and evaporate the solution on the water-bath. Towards the end of the operation add a few more drops of hydrochloric acid, and keep the residue on the water-bath, until no more hydrochloric acid vapors escape. Determine now the chlorine in the residue (§ 141), calculate from this the alkali, and you will find the boracic acid from the difference.

E. SCHWEIZER, with whom this method originated, states that it gave him very satisfactory results in the analysis of borax. It will answer also for the estimation of the bases in the case of some other borates. It is self-evident that the boracic acid may be estimated, in another portion of the salt, by I., 1, *c*, or 2. If you have to estimate boracic acid in presence of large proportions of alkaline salts, make the fluid alkaline with potassa, evaporate to dryness, extract the residue with alcohol and some hydrochloric acid, add solution of potassa to strongly alkaline reaction, distil off the spirit of wine, and then proceed as in I., 1, *c*, or 2 (AUG. STROMEYER, *loc. cit.*).

b. From almost all other Bases.

The compounds are decomposed by boiling or fusing with carbonate or hydrate of potassa; the precipitated base is filtered off, and the boracic acid determined in the filtrate, according to the directions of I., 1, *c*, or 2. If magnesia was present, a little of this is very likely to get into the filtrate, and—if process I., 2, is employed—upon neutralizing with hydrofluoric acid, this separates as insoluble fluoride of magnesium, which may either be filtered off at once, or removed subsequently, by treating the boro-fluoride of potassium with boiling water, in which that salt is soluble, and the fluoride of magnesium insoluble.

c. From the Metallic Oxides of the Fourth, Fifth and Sixth Groups.

The metallic oxides are precipitated by sulphuretted hydrogen, or, as the case may be, sulphide of ammonium, and determined by the appropriate methods. The quantity of boracic acid may often be inferred from the loss. If it has to be estimated in the direct way, the filtrate, after addition of solution of potassa and some nitrate of potassa, is evaporated to dryness, the residue ignited, and the boracic acid estimated by I., 1 *c*, or 2. In cases where the metal has been precipitated by sulphuretted hydrogen from acid or neutral solutions, the boracic acid may also be determined in the filtrate—in the absence of other acids—by I., 1 *a* or *b*, after the complete removal of the sulphuretted hydrogen by transmitting carbonic acid through the fluid.

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* Annal. d. Chem. u. Pharm. 100, 82.

d. From the whole of the Fixed Bases.

A portion of the very finely pulverized compound under examination is weighed, put into a capacious platinum dish, and digested with a sufficient quantity of hydrofluoric acid; pure concentrated sulphuric acid is then gradually added, drop by drop, and the mixture heated, gently at first, then more strongly, until the excess of the sulphuric acid is completely expelled. In this operation the boracic acid goes off in the form of fluoride of boron ($B\ O_3 + 3\ H\ Fl = B\ Fl_3 + 3\ H\ O$). The residue contains the bases in the form of sulphates; the bases are determined by the appropriate methods, and the quantity of the boracic acid is inferred from the difference between the weight of the separated base and that of the analyzed borate. The application of this method presupposes, of course, that the analyzed compound is decomposable by sulphuric acid.

§ 137.

3. OXALIC ACID.

I. *Determination.*

Oxalic acid is either precipitated as *oxalate of lime*, and the latter determined as *carbonate of lime;* or the amount contained in a compound is inferred from the quantity of solution of permanganate of potassa required to effect the conversion into carbonic acid; or from the quantity of gold which it reduces; or from the amount of carbonic acid which it yields upon accession of 1 eq. oxygen.

a. Determination as Carbonate of Lime.

Precipitate with solution of acetate of lime, added in moderate excess, and treat the precipitated oxalate of lime as directed in § 103. If this method is to yield accurate results, the solution must be neutral or slightly acid with *acetic acid;* it must not contain alumina, sesquioxide of chromium, or oxides of the heavy metals, more especially sesquioxide of iron or oxide of copper; therefore, where these conditions do not exist, they must first be supplied.

b. Determination by means of Solution of Permanganate of Potassa.

Determine the strength of the solution of permanganate of potassa, as directed p. 196, *cc*, by means of oxalic acid; then dissolve the compound in which the oxalic acid is to be estimated, and which must be free from all other bodies that might act on solution of permanganate of potassa, in 400 or 500 parts of water, or, as the case may be, acid and water; add, if necessary, a further, not too small, quantity of sulphuric acid, heat to about 60°, and then add the permanganate, drop by drop, with constant stirring, until the fluid just shows a red tint (compare p. 196). Knowing the quantity of oxalic acid which 100 c. c. of the standard permanganate will oxidize, a simple calculation will give the quantity of oxalic acid corresponding to the c. c. of permanganate used in the experiment. The results are very accurate.

c. Determination from the reduced Gold (H.ROSE).

α. In Compounds soluble in Water.

Add to the solution of the oxalic acid or the oxalate a solution of sodio-terchloride, or ammonio-terchloride of gold, and digest for some time at a temperature near ebullition, with exclusion of direct sunlight. Collect the precipitated gold on a filter, wash, dry, ignite, and weigh. 1 eq. gold (196) corresponds to 3 eq. $C_2 O_3$ ($3 \times 36 = 108$).

β. In Compounds insoluble in Water.

Dissolve in the least possible amount of hydrochloric acid, dilute with a very large quantity of water, in a capacious flask, cleaned previously with solution of soda; add solution of gold in excess, boil the mixture some time, let the gold subside, taking care to exclude sunlight, and proceed as in *α*.

d. Determination as Carbonic Acid.

This may be effected either,

α. By the method of organic analysis (§ 174); or,

β. By mixing the oxalic acid or oxalate with finely pulverized binoxide of manganese in excess, and adding sulphuric acid to the mixture, in an apparatus so constructed that the disengaged carbonic acid passes off perfectly dry.

The theory of this method may be illustrated by the following equation:

$$C_2 O_3 + Mn O_2 + S O_3 = Mn O, S O_3 + 2 C O_2$$

For each 1 eq. oxalic acid we obtain accordingly 2 eq. carbonic acid. For the apparatus and process, I refer to the chapter on the examination of manganese ores, in the special part of this work. Here I may remark that free oxalic acid must first be prepared for the process by slight supersaturation with ammonia, and also that 9 parts of anhydrous oxalic acid require theoretically 11 parts of (pure) binoxide of manganese. Since an excess of the latter substance does not interfere with the accuracy of the results, it is easy to find the amount to be added. The binoxide of manganese need not be pure, but it must contain no carbonate. This method is expeditious, and gives very accurate results, if the process is conducted in an apparatus sufficiently light to admit of the use of a delicate balance.

Instead of binoxide of manganese, chromate of potassa may be used; (compare § 130, *c.*)

II. *Separation of Oxalic Acid from the Bases.*

The most convenient way of analyzing oxalates is, in all cases, to determine in one portion, the acid, by one of the methods given in I., in another portion, the base, particularly as the latter object may be generally effected by simple ignition in the air, which reduces the salt either to the metallic state (*e. g.*, oxalate of silver), or to pure oxide (*e. g.* oxalate of lead), or to carbonate (*e. g.*, the oxalates of the alkalies and alkaline earths.)

If acid and base have to be determined in one and the same portion of the oxalate, the following methods may be resorted to:

a. The oxalic acid is determined by I., *c*, and the gold separated from the bases in the filtrate by the methods given in Section V.

b. In many soluble salts the oxalic acid may be determined by the method I., *a*; separating the bases afterwards from the excess of the salt of lime by the methods given in Section V.

c. Many oxalates whose bases are precipitated by carbonate of potassa or carbonate of soda, and are insoluble in an excess of the precipitant, may be decomposed by boiling with an excess of solution of carbonate of potassa or carbonate of soda, oxide or carbonate being formed on the one, and alkaline oxalate on the other side.

d. All salts of oxalic acid with the oxides of the fourth, fifth, and sixth groups, may be decomposed with sulphuretted hydrogen, or sulphide of ammonium.

§ 138.

4. Hydrofluoric Acid.

I. *Determination.*

Free hydrofluoric acid in aqueous solution is best determined as *fluoride of calcium.* For this purpose, carbonate of soda is added in moderate excess, then a solution of chloride of calcium as long as a precipitate continues to form; when the precipitate, which consists of fluoride of calcium and carbonate of lime, has subsided, it is washed, first by decantation, afterwards on the filter, and dried; when dry, it is ignited in a platinum crucible (§ 53); water is then poured over it, in a platinum or porcelain dish, acetic acid added in slight excess, the mixture evaporated to dryness on the water-bath, and heated on the latter until all odor of acetic acid disappears. The residue, which consists of fluoride of calcium and acetate of lime, is heated with water, the fluoride of calcium filtered off, washed, dried, ignited (§ 53), and weighed. If the precipitate of fluoride of calcium and carbonate of lime were treated with acetic acid, without previous ignition, the washing of the fluoride would prove a difficult operation. Presence of nitric or hydrochloric acid in the aqueous solution of the hydrofluoric acid does not interfere with the process (H. Rose).

II. *Separation of Fluorine from the Metals.*

a. Soluble Fluorides.

If the solutions have an acid reaction, carbonate of soda is added in excess. If this produces no precipitate, the fluorine is determined by the method given in I., and the bases in the filtrate are separated from the excess of lime, and from the soda, by the methods given in Section V. But if the carbonate of soda produces a precipitate, the mixture is heated to boiling, then filtered, and the fluorine determined in the filtrate by the method given in I.; the base is in the residue, which must, however, first be tested, to make sure that it contains no fluorine. Neutral solutions are mixed with a sufficient quantity of chloride of calcium, and the mixture heated to boiling in a platinum dish, or, but less appropriately, in a porcelain dish; the precipitate of fluoride of calcium is allowed to subside, thoroughly washed with hot water by decantation, transferred to the filter, dried, ignited, and weighed. The bases in the filtrate are then separated from the excess of the salt of lime by the usual methods. That the bases may be determined also in separate portions by the methods given in *b*, need hardly be stated.

b. Insoluble Fluorides.

a. Anhydrous insoluble Fluorides.

The finely pulverized and accurately weighed substance is heated for some time with pure concentrated sulphuric acid, and finally ignited until the free sulphuric acid is completely expelled. The residuary sulphate is weighed, and the metal contained in it calculated. The difference between the calculated weight of the metal and that of the original fluoride shows the amount of fluorine originally present in the analyzed compound. In cases where we have to deal with a metal whose sulphate gives off part of the sulphuric acid upon ignition, or where the residue contains several metals, it is necessary to subject the residue to analysis before this calculation can be made.

β. Hydrated insoluble Fluorides.

A sample of the compound under examination is heated in a tube.

aa. The Water expelled does not redden Litmus Paper.

In this case the amount of water present is ascertained by igniting the hydrated compound, and the fluorine and metal are subsequently determined as directed in II., *b. α.*

bb. The Water expelled has an acid reaction.

The fluoride under examination is, in the first place, treated with sulphuric acid, as directed in II., *b*, *α*, to determine the metal on the one hand, and the water + fluorine on the other. Another weighed portion is then mixed, in a small retort, with about 6 parts of recently ignited oxide of lead; the mixture is covered with a layer of oxide of lead, the retort weighed, and the water expelled by the application of heat, increased gradually to redness. No hydrofluoric acid escapes in this process. The weight of the expelled water is inferred from the loss. The first operation having given us the water + fluorine, and the second, the water alone, the difference is consequently the fluorine.

In the fifth section we shall have occasion to speak of another method of determining fluorine (in the chapter on the separation of fluorine from silicic acid).

Fourth Division of the First Group of the Acids.

CARBONIC ACID—SILICIC ACID.

§ 139.

1. CARBONIC ACID.

I. *Determination.*

a. In a mixture of Gases.

After thoroughly drying the gases with a ball of chloride of calcium, measure them accurately, in a graduated tube over mercury, insert a moistened ball of hydrate of potassa, cast on a platinum wire in a pistol bullet-mould, and leave this in the tube for 24 hours, or until the volume of the gas ceases to show further diminution; withdraw the ball, and measure the gas remaining, re-insert the same or a fresh moistened ball of potassa and repeat till no further absorption takes place. The carbonic acid gas is inferred from the difference, provided the gaseous mixture contained no other gas liable to absorption by potassa (compare §§ 12–16).

If the amount of carbonic acid is very small, this process does not yield sufficiently accurate results. In such cases one of the methods recommended for the estimation of carbonic acid in atmospheric air (see § 241) should be employed.

b. In Aqueous Solution.

α. WITH HYDRATE OF LIME.

Into a flask, holding about 300 c. c. and provided with a good india-rubber cork, put 2 to 3 grm. hydrate of lime perfectly free from carbonate,* tare or weigh exactly, add the carbonic acid water, cork immediately and weigh again. (If the water is measured with a plunging syphon, of course this mode of ascertaining the amount of water employed is superfluous.) Heat the contents of the flask for some time in a water-bath (raising the cork every now and then) to hasten the conversion of the amorphous carbonate of lime into the crystalline, and pour off the clear fluid as completely as possible without disturbing the precipitate through a small ribbed filter. This operation is soon finished, and the filter is at once—without washing—thrown into the flask containing the precipitate and the rest of the fluid; the carbonic acid is determined now according to II., *e*; or, if the carbonic acid water contains bicarbonate of an alkali, it is well to add, besides the hydrate of lime, also enough chloride of calcium to decompose the alkaline carbonate.

β. AFTER PETTENKOFER. †

The principle of this simple and expeditious process consists in mixing the carbonic acid water with a measured quantity of standard lime-water (or, under certain circumstances, baryta water) in excess. After complete separation of the carbonate of lime the excess of alkaline earth in the fluid is determined in an aliquot part by means of standard solution of oxalic acid; the difference gives the lime precipitated by the carbonic acid, and consequently the amount of the latter present.

If a water contains only free carbonic acid, the analyst has only to bear in mind that the carbonate of lime formed is at first, as long as it remains amorphous, very perceptibly soluble in water, to which it communicates an alkaline reaction. Hence the unprecipitated lime in the fluid cannot be estimated till the carbonate of lime has separated in the crystalline form—this takes 8 or 10 hours if the mixture is not warmed to 70° or 80°.

If, on the contrary, a water contains an alkaline carbonate or any other alkaline salt whose acid would be precipitated by lime, a neutral solution of chloride of calcium must first be added to decompose the same. This addition, too, prevents any inconvenience arising from the presence of free alkali in the lime-water or of carbonate of magnesia in the carbonic acid water; this inconvenience consists in the fact that oxalate of an alkali or of magnesia enters into double decomposition with carbonate of lime (which is never entirely absent from the fluid to

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* This is prepared by slaking freshly burnt lime with water in such a manner that the hydrate obtained appears dry and pulverulent. Should it contain carbonic acid (as may be seen by putting a portion into hydrochloric acid) it is ignited in a current of air free from carbonic acid in a tube of difficultly fusible glass placed in a combustion furnace.

† Buchner's neues Repert. 10, 1.

[illegible] oxalate of lime and carbonate of the alkali or of [illegible] which latter will of course again take up oxalic acid.

In the presence of magnesia salts in carbonic acid water, in order to [illegible] the precipitation of the magnesia, a little chloride of ammonium [illegible] be added, but in this case heat must not be applied to induce [illegible] bonate of lime to become more quickly crystalline, as ammonia [illegible] be thereby expelled.

In making the determination, the first thing to be done is to ascertain the relation between the lime water and a standard solution of oxalic acid. PETTENKOFER makes the latter solution by dissolving 2·8636 grm. pure unaffloresced dry crystallized oxalic acid to 1 litre; 1 c. c. of this is equivalent to 1 mgrm. carbonic acid. The lime water is standardized as follows: measure 45 c. c. into a little flask which can be closed by the thumb, and then run in from the burette the solution of oxalic acid till the alkaline reaction has just vanished. During the operation the flask is closed with the thumb and gently shaken. The end is attained as soon as a drop taken out with a glass rod and applied to delicate turmeric paper produces no brown ring. The first experiment is a rough one, the second should be exact.

The analysis of a carbonic acid water (a spring water, for instance) is performed by transferring 100 c. c. to a dry flask, adding 3 c. c. of a neutral and nearly saturated solution of chloride of calcium and 2 c. c. of a saturated solution of chloride of ammonium, then 45 c. c. of the standard lime water; close the flask with an india-rubber cork, shake and allow to stand 12 hours. The fluid contents of the flask measure consequently 150 c. c. From the clear fluid take out by means of a pipette two portions of 50 c. c. each, and determine the free lime by means of oxalic acid, in the first portion approximately, in the second exactly. Multiply the c. c. used in the last experiment by 3 and deduct the product from the c. c. of oxalic acid which correspond to 45 c. c. of lime water. The difference shows the lime precipitated by carbonic acid; each c. c. corresponds to 1 mgrm. carbonic acid.

The method is convenient and good; it is especially to be recommended for dilute carbonic acid water. In water containing much carbonic acid it is well to replace the lime- by baryta water; compare the determination of carbonic acid in atmospheric air, § 241.

II. *Separation of Carbonic Acid from the Bases, and its Estimation in Carbonates.*

a. Separation from Neutral Carbonates of Alkalies and the Alkaline Earths.

If the salts contain unquestionably 1 eq. carbonic acid to 1 eq. base, and there is no other salt with alkaline reaction present, we may determine the quantity of the base by the alkalimetric method (§§ 207, 208, 201), and calculate for each 1 eq. base 1 eq. carbonic acid.

b. Separation from Bases which upon Ignition readily and completely yield the Carbonic Acid with which they are combined.

Such are, for instance, the carbonates of zinc, cadmium, lead, copper, magnesia, &c.

α. Anhydrous Carbonates.

Ignite the weighed substance in a platinum crucible (carbonates of cadmium and lead in a porcelain crucible), until the weight of the residue remains constant. The results are, of course, very accurate. Substances liable to absorb oxygen upon ignition in the air are ignited in a bulb-tube, through which a stream of dry carbonic acid gas is conducted. The carbonic acid is inferred from the loss.

β. *Hydrated Carbonates.*

The substance is ignited in a bulb-tube through which dried air, or, in presence of oxidizable substances, carbonic acid is transmitted, and which is connected with a chloride of calcium tube, by means of a dry, close-fitting cork. During the ignition, the posterior end of the bulb-tube is, by means of a small lamp, kept sufficiently hot to prevent the condensation of water in it, care being taken, however, to guard against burning the cork. The loss of weight of the tube gives the amount of the water + the carbonic acid; the increase of weight gained by the chloride of calcium tube gives the amount of the water, and the difference accordingly that of the carbonic acid. A somewhat wide glass tube may also be put in the place of the bulb-tube, and the substance introduced into it in a little boat, which is weighed before and after the operation.

c. Separation from all Bases, without exception, in Anhydrous Carbonates.

Fuse vitrified borax in a weighed platinum crucible, allow to cool in the desiccator, weigh, then transfer the well-dried substance to the crucible and weigh again. The weights of both carbonate and borax are thus ascertained. They should be in about the proportion of 1 : 4. Heat is then applied, which is gradually increased to redness, and maintained at this temperature until the contents of the crucible are in a state of calm fusion. The crucible is now allowed to cool, and weighed. The loss of weight is carbonic acid. The results are very accurate (SCHAFFGOTSCH).

I must add that borax-glass may be kept in a state of fusion at a red heat for ¼ to ½ an hour without the occurrence of any volatilization, but that at a white heat (by igniting over the gas-bellows), even in a few minutes, it suffers a decided loss.* A few bubbles of carbonic acid remaining in the fusing mass are without any influence on the result.

d. Separation from all Bases without exception.

(*Estimation of the Acid from the loss of weight.*)

aa. Carbonates whose Bases form Soluble Salts with Sulphuric Acid.

The process is conducted in the apparatus illustrated by fig. 53.

The size of the flasks depends upon the capacity of the balance which the operator possesses. The tube *a* is closed at *b* by means of a small wax stopper; † the other end of the tube *a* is open, as are also both ends of *c* and *d*. The flask *B* is nearly half filled with concentrated sulphuric acid; the tubes must fit air-tight in the perforations of the corks, and the latter equally so in the mouths of the flasks. The weighed substance is put into *A*; this flask is then filled about one-third with water, the cork properly inserted, and the apparatus tared on the balance.

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* Zeitschrift f. analyt. Chem. 1, 65.

† Or with a small piece of india-rubber tube, drawn over it, and having inserted in the other end a short piece of glass rod.

A few bubbles of air are now sucked out of *d*, by means of a small india-rubber tube. This serves to rarefy the air in *A* also, and causes the sulphuric acid in *B* to ascend in the tube *c*. The latter is watched for some time, to ascertain whether the column of sulphuric acid in it remains stationary, which is a proof that the apparatus is air-tight. Air is then again sucked out of *d*, which causes a portion of the sulphuric acid to flow over into *A*. The carbonate in the latter flask is decomposed by the sulphuric acid, and the liberated carbonic acid, completely dried in its passage through the concentrated sulphuric acid in *B*, escapes through *d*. When the evolution of the gas slackens a fresh portion of sulphuric acid is made to pass over into *A*, by renewed suction through *d*; and the same operation is repeated until the whole of the carbonate is decomposed. A more vigorous suction is now applied, to make a larger amount of sulphuric acid pass over into *A*, whereby the contents of that flask are considerably heated; when the evolution of gas bubbles has completely ceased, the wax stopper on *a* is opened, or the glass rod removed from the india-rubber cap, and suction applied to *d*, until the air sucked out tastes no longer of carbonic acid.*

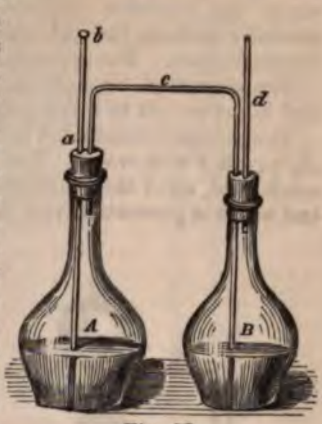

Fig. 53.

After about 3 hours, the apparatus is replaced upon the balance, and the equilibrium restored by additional weights. The sum of the weights so added indicates the amount of carbonic acid originally present in the substance.

If the flasks *A* and *B* are selected of small size, the apparatus may be so constructed that, together with the contents, it need not weigh above seventy grammes, admitting thus of being weighed on a delicate balance. The results obtained by the use of this apparatus, first suggested by Will and myself, are very accurate, provided the quantity of the carbonic acid be not too trifling. Manifold modifications of the apparatus have been proposed, principally in order to make it lighter. See Geissler's Apparatus, p. 291.

If sulphites or sulphides are present, together with the carbonates, their injurious influence is best obviated by adding to the carbonate solution of yellow chromate of potassa in more than sufficient quantity to effect their oxidation. If chlorides are present, in order to prevent the evolution of hydrochloric acid, add to the evolution flask a sufficient quantity of sulphate of silver in solution, or connect the exit tube *d* with a small prepared U-tube, which is, of course, first tared with the apparatus, and afterwards weighed with it. This U-tube is prepared—in accordance with the happy proposal of Stolba—by filling with fragments of pumice which have been boiled with an excess of concentrated solution of sulphate of copper, till the air has been expelled, and then dried and heated to complete dehydration of the copper salt. If the U-tube is only 8 cm. high and has an internal diameter of 1 cm., it answers the purpose very well. The end not connected with *d* is provided with a perforated cork and short glass tube. We apply suction to this by means of a flexible tube, instead of to *d*.

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* In accurate experiments, it is advisable to connect the end *b* of the tube *a* with a chloride of calcium tube during the process of suction.

bb. Carbonates whose Bases form insoluble Salts with Sulphuric Acid. The analysis of such carbonates cannot well be effected by the method *aa*, as the insoluble sulphate formed (sulphate of lime, for instance) partially protects the yet undecomposed portion of the carbonate from decomposition. The apparatus is therefore modified as shown in fig. 54.

The alteration consists simply in the tube *a*, which contains a bulb, and is drawn out to a fine point at the lower end.

The process is conducted as follows: The weighed substance is put into *A*, together with water. The bulb-tube *a* contains an amount of dilute nitric acid, more than sufficient for the decomposition of the carbonate, and which is prevented from flowing through the narrow aperture of this tube by the little wax stopper *b*.* The point of this tube must not at first dip into the water in *A*. The apparatus having been tared on the balance, the tube *a* is carefully and cautiously moved down, until its point nearly touches the bottom of *A*. The wax stopper *b* is then momentarily raised, or the glass rod removed from the india-rubber cap, so as to allow a small quantity of nitric acid to flow out of the tube *a*; and the same operation is repeated, until the carbonate is completely decomposed. The contents of *A* are then heated to incipient boiling, the stopper at *b* removed, and the carbonic acid sucked out of the apparatus as directed in *aa*. The diminution of weight is ascertained when the apparatus is completely cooled.

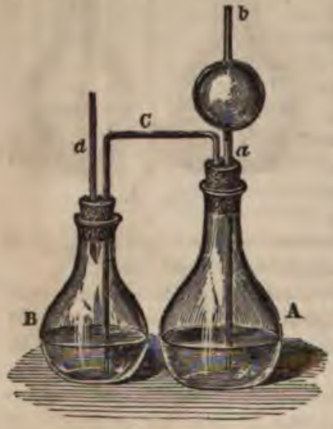

Fig. 54.

It will be seen at a glance that a different construction may also be given to the apparatus; that, for instance, the tube *C* may be connected, instead of with *B*, with a chloride of calcium tube, or with a tube filled with pumice stone or asbestos moistened with sulphuric acid; also, that the substance to be analyzed may be put into a small tube, which stands upright at first, or is suspended from a thread, but is subsequently, after taring the apparatus, upset or lowered into the dilute acid in the flask; also, that the closing of *a* may be effected by means of a compression clamp, &c.

The apparatus proposed by GEISSLER † is very convenient (see fig. 55). It consists of two parts, *A B* and *C*. *C* is ground into the neck of *A* (*a*), so as to close air-tight, and yet admit of being readily removed, for the purpose of filling and emptying *A*. *b c* is a glass tube, open at both ends, and ground water-tight into *C*, at the lower end (*c*); it is kept in the proper position by means of an easily movable cork, *i*. The illustration shows the construction of the apparatus in other respects. The cork *e* must fit air-tight, as must the tube *d* in the cork. The weighed substance is put into *A*, water added to the extent indicated in the engraving, and the substance shaken towards the side of the flask. *C* is now filled nearly to the top with dilute nitric acid, with the aid of a pipette, after having previously turned the cork *i* upwards, without raising *b*; the cork is then again twisted down again, and *C* inserted into *A*; *B* is filled somewhat more than half with concentrated sulphuric acid, and *b* closed at the top with a little wax stopper, or a piece of india-rubber tube, with a small glass rod inserted in it. After taring the apparatus, the decomposition is effected by raising *b* a little, and thus causing acid to pass from *C* into *A*. The carbonic acid escapes through *h* into the sulphuric acid, where it is dried; it then leaves the apparatus through *d*. After the decomposition has been effected, *A* is cautiously heated to incipient boiling, the stopper on *b* opened, and the carbonic acid still remaining in the apparatus sucked out through *d* by means of a small india-rubber tube. The apparatus is finally weighed when cold.

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* Or india-rubber cap, with glass rod. See note, p. 288

† Journ. f. prakt. Chem. 60, 35.

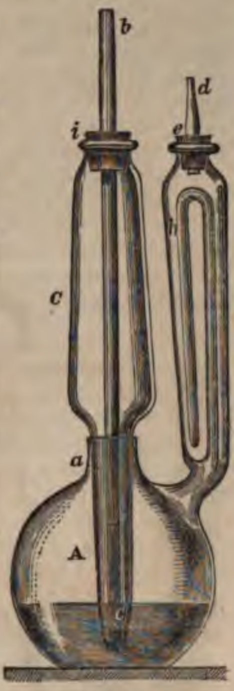

Fig. 55.

If you prefer to decompose the carbonate with hydrochloric acid, dry the escaping gas with the pumice-stone saturated with anhydrous sulphate of copper (see *aa*), which also retains hydrochloric acid as well as the moisture (STOLBA*). It is well to fill a light U-tube with this material. The size of the U-tube should depend on the size of the apparatus. It can be used as long as a third of its contents remains uncolored.

[*cc. Carbonates which dissolve freely in cold-dilute acid.*†

In the processes hitherto described, carbonic acid is determined by the loss of weight of an apparatus which contains no carbonic acid gas at the beginning and which must be completely emptied of this gas at the conclusion of the analysis. It is a matter of experience, however, that accurate results are not attainable with certainty in this way. Nothing short of actual boiling for some time will expel all carbonic acid gas from the dilute acid liquid. This cannot be done conveniently without loss of aqueous vapor. The fact that good results are often obtained is due to the compensation of opposite errors, as the analyst may convince himself by repeatedly heating and sucking through air. If the suction go on to just the right extent, the loss of the apparatus will exactly correspond to the carbonic acid that was contained in the substance, but further exhaustion of the air will diminish the weight of the apparatus, not by complete removal of the carbonic acid, but by loss of aqueous vapor, which easily escapes the desiccating material. By continued working on a carbonate of known composition one may soon learn how long to exhaust in order to bring out the proper loss, but where the analyst is

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[*] Dingler's pol. Journ. 164, 128.

[†] American Journal of Science and Arts, Vol. xlviii., July, 1869.

out of practice, an error of 1 to 2 per cent. is not unlikely to happen, and the process itself furnishes no means of judging when it will give a correct result.

The editor employs a simple modification of this method, which, under proper conditions, gives very accurate results and furnishes to a great extent its own control. The process is novel in this particular, viz.: the charged apparatus is in the first place filled with carbonic acid gas, the substance is then decomposed, and as soon as disengagement of gas ceases, the apparatus, still filled with carbonic acid gas, is weighed again. In this manner all aspiration is done away with, and the desiccating material has simply to dry as much gas as is yielded by the substance under analysis.

It is, however, essential that the substance under examination dissolve freely and completely in cold acid; it is likewise necessary that the analysis and weighings be conducted in an apartment not liable to change of temperature.

The apparatus may consist of a light flask or bottle with wide mouth which is closed by a soft rubber stopper, through which there passes, on the one hand, a chloride of calcium tube, the lower bulb of which contains cotton, and, on the other, the neck of a vessel which contains the dilute acid. This acid reservoir is so constructed that on suitably inclining it, its contents will flow freely into the flask. For this purpose the tube connecting with the latter has an internal diameter of seven millimetres, and its extremity is cut off obliquely; at its other end, the acid reservoir terminates in an upturned narrow tube, *b*. This and the upper termination of the CaCl tube are chosen of such diameter that they fit quite snugly into short, narrow and thick-walled rubber connectors which are again provided with glass-rod stoppers; all these joints must be gas-tight. In figure 56 the apparatus is represented in one-third its proper dimensions.

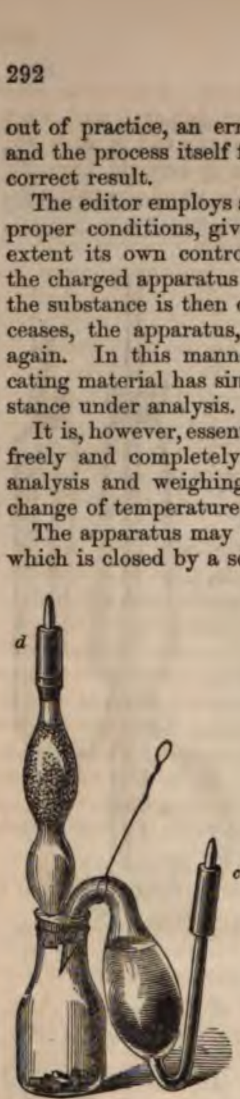

Fig. 56.

The weighed substance, in case of carbonate of lime, *e. g.*, is placed at the bottom of the flask, most conveniently in the form of small fragments. The acid vessel is nearly filled with hydrochloric acid of sp. gr. 1·1. It and the CaCl tube are tightly adjusted to the neck of the flask, and the glass-rod stoppers being removed, the apparatus is connected at *c* with a self-regulating generator of washed carbonic acid, and a rather rapid stream of the gas is transmitted through the apparatus for 15 minutes, or until the liquid in *b* is saturated and the air is thoroughly displaced. Then the opening at *d* is stopped and afterward the apparatus is disconnected with the carbonic acid generator and stopped at *c*. During these as well as the subsequent operations, the apparatus must be so handled that its temperature shall not change. It is immediately weighed. When removed from the balance, loosen the stopper at *d*, and, holding the flask by a wooden clamp, incline it so that the acid may flow over upon the carbonate. The decomposition should proceed slowly, so that the escaping gas may be thoroughly dried. As soon as solution of the carbonate is complete, replace the stopper at *d*, and weigh again. Should there be any leak in the apparatus the fact is made evident by a slow but steady loss of weight, when it is brought upon the balance. If all the joints are sufficiently tight, the weight remains the same for at least fifteen minutes.

When properly executed the process gives extremely accurate results; a slight change of temperature or of atmospheric pressure between the two weighings of course greatly impairs the results or renders them worthless. Since the apparatus usually rises a little in temperature during the solution of the carbonate, it is better, as soon as the substance is decomposed, to stopper the CaCl tube and let the whole stand fifteen minutes, then to connect as before with the gas-generator and pass *dried* CO_2 for a minute, and finally to stopper again and bring upon the balance. In seven analyses of pure calcite in quantities ranging from 0·5 to 0·9 grm., the editor obtained the following percentages of carbonic acid, viz.: 44·07, 44·07, 43·98, 44·01, 44·04, 44·11, 44·16; calculation requires 44·00.

In case of alkali-carbonates which absorb carbonic acid gas, it is necessary to modify the apparatus. Instead of the light flask *a*, we may employ a small bottle of thick glass and wider mouth, and a thrice-perforated rubber stopper. Through the third orifice pass a narrow tube 3 to 4 inches long enlarged below to a small bulb to contain the carbonate. This bulb must be so thin that on pushing down the tube within the bottle it shall be easily crushed to pieces against the bottom of the latter. The carbonate is weighed into the bulb-tube, the latter is wiped clean, down to the bulb, corked and fixed in the stopper. The apparatus is filled as before with CO_2 and weighed. Then the bulb is broken and the process finished as before described. In three estimations on carbonate of soda the editor found 41·54, 41·64 and 41·58 per cent. of CO_2. Calculation requires 41·51 per cent.]

e. From all Bases without exception (Estimation of the Acid from the increase of weight of an Absorption Apparatus).

The arrangement of the apparatus I employ will be seen from fig. 57. *a* is the evolution flask (300 c. c.) closed with a doubly-perforated india-rubber cork, *bb* is a tube twice bent and expanded at *c* to a small bulb, it may be connected by means of an india-rubber tube as required either with the little funnel *d*, or with the tube *e*, which is filled with soda-lime or hydrate of potassa. The U-tube *f* is filled, as regards the bulbed limb, with pieces of fused chloride of calcium; as regards the other limb, with fragments of pumice saturated with anhydrous sulphate of copper (see p. 289). The U-tube *g* contains pieces of glass, 6—10 drops of concentrated sulphuric acid, and two little asbestos stoppers, the tube *h* is ⅞ filled with about 20 grm. coarsely granulated soda-lime, and towards the outer end the remaining ⅛ is filled with coarsely granulated chloride of calcium, *k* contains in the outward limb soda-lime, in the inner, chloride of calcium. *f* serves to free the escaping carbonic acid from moisture and hydrochloric acid, *g* enables the operator to see the rate of the evolution of gas, *h*, by its soda-lime, takes up the carbonic acid completely, and by its chloride of calcium prevents any evaporation of water from the former (the soda-lime gets warm on absorbing the carbonic acid), *k* serves to protect the tube *h* (which has to be weighed) from any moisture, &c., which might penetrate from outside. The corks of *g*, *h* and *k* must be covered with sealing-wax.* The absorption apparatus is that given by Mulder,† and is here especially suitable, as the carbonic acid is mixed with much air, and the evolution is at times somewhat rapid.

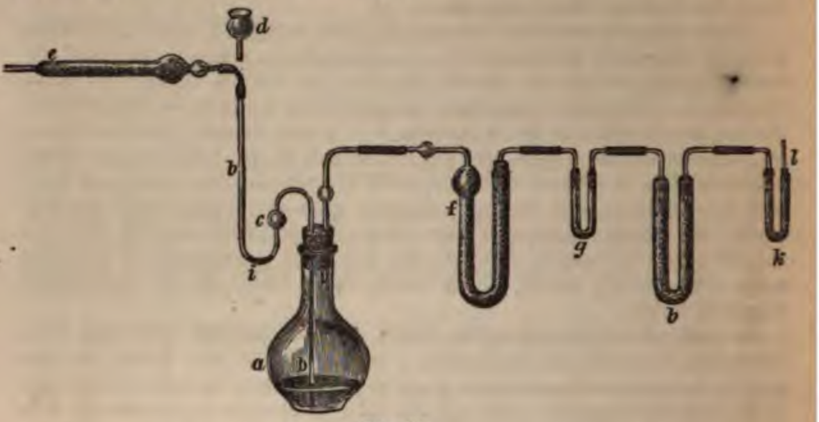

Fig. 57.

After the weighed substance has been transferred to *a*, and a little water has been added to it, weigh *h* and *g* together, and connect the several parts of the apparatus—*a* stands on a wire gauze, placed on a tripod, *e* is fastened to a support, the U-tubes are suspended in a suitable manner—join *b* to *d*, and pour into *d* a small portion of mercury, just enough to close the tube at *i*. Now pour into *d* common hydrochloric or nitric acid (previously diluted with an equal bulk of water), and by gentle suction through an india-rubber tube at *l* cause a small quantity of acid to flow into the flask *b*. The evolution of carbonic acid commences immediately; its rate may be seen from *g*; if necessary, a gentle heat may be applied. When the evolution begins to abate, introduce more acid into the flask in the same manner as before. As soon as the carbonate is perfectly decomposed, fill *d* several times with hot water, causing it to flow into *a*. This is done in order to wash into *a* the small quantities of hydrochloric acid which remain in *c*, and which possibly might have taken up some carbonic acid. Now remove *d* and connect *e* with *b* instead, heat the contents of *a* to gentle boiling, which is to be continued till the first bulb of *f* is hot, and then by sucking at *l*, draw air through the apparatus to the extent of six times the volume that *a* contains. This suction is best effected by an aspirator. When this has been done, separate *a* from *f*, allow *h* to cool completely, remove *h* and *g*, and weigh them together. The increase of weight of these is the exact expression of the carbonic acid in the substance. The accuracy of the results leaves nothing to be desired. We have the bases without any impurity, and completely dissolved in hydrochloric or nitric acid.

The tube *g* is, after use, closed at both ends, and retains its utility a long

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* Or caoutchouc stoppers may be used. For small U-tubes, half an inch of fleshy india-rubber tubing forms an excellent joint.

† Zeitschrift f. analyt. Chem. 1, 2.

I. TABLE OF THE ABSORPTION OF CARBONIC ACID

in 5 c. c. of H Cl., sp. gr. 1·125, for an evolution of 1 to 100 c. c.

Evolved......	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Absorbed.....	1.85	2.00	2.16	2.31	2.47	2.62	2.78	2.93	3.09	3.24	3.40	3.55	3.71	3.86	4.02	4.17	4.33	4.48	4.64	4.79
Evolved......	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
Absorbed.....	4.95	4.96	4.97	4.98	5.00	5.03	5.04	5.06	5.07	5.09	5.10	5.11	5.13	5.14	5.16	5.17	5.18	5.20	5.21	5.23
Evolved......	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Absorbed.....	5.24	5.25	5.26	5.27	5.28	5.30	5.31	5.32	5.34	5.35	5.36	5.37	5.38	5.48	5.41	5.43	5.44	5.45	5.47	5.48
Evolved......	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80
Absorbed.....	5.50	5.51	5.52	5.54	5.55	5.57	5.58	5.59	5.61	5.62	5.64	5.65	5.66	5.68	5.69	5.71	5.72	5.73	5.75	5.76
Evolved......	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
Absorbed.....	5.78	5.79	5.80	5.82	5.83	5.85	5.86	5.87	5.89	5.90	5.92	5.93	5.94	5.96	5.97	5.99	6.00	6.01	6.03	6.04

TABLE OF THE WEIGHT OF A CUBIC

in Milligrammes from 720 *to* 770 *mm. of pressure*

MILLIMETRES.

TEMPERATURE CENT.	720	722	724	726	728	730	732	734	736	738	740	742	744
10°	1.77446	1.77945	1.78445	1.78944	1.79443	1.79942	1.80441	1.80941	1.81440	1.81940	1.82438	1.82937	1.83437
11°	1.76668	1.77165	1.77662	1.78160	1.78657	1.79155	1.79652	1.80149	1.80647	1.81144	1.81642	1.82139	1.82636
12°	1.75881	1.76377	1.76873	1.77368	1.77864	1.78359	1.78855	1.79351	1.79846	1.80342	1.80838	1.81333	1.81829
13°	1.75092	1.75587	1.76081	1.76576	1.77070	1.77565	1.78059	1.78554	1.79048	1.79543	1.80037	1.80532	1.81026
14°	1.74301	1.74795	1.75288	1.75781	1.76275	1.76768	1.77261	1.77754	1.78248	1.78741	1.79234	1.79728	1.80221
15°	1.73502	1.73993	1.74484	1.74974	1.75465	1.75955	1.76446	1.76937	1.77427	1.77918	1.78408	1.78899	1.79390
16°	1.72699	1.73188	1.73677	1.74166	1.74655	1.75144	1.75633	1.76122	1.76611	1.77100	1.77590	1.78078	1.78567
17°	1.71888	1.72376	1.72862	1.73349	1.73836	1.74322	1.74809	1.75296	1.75783	1.76269	1.76756	1.77243	1.17729
18°	1.71069	1.71554	1.72040	1.72525	1.73011	1.73497	1.73982	1.74468	1.74953	1.75439	1.75925	1.76410	1.76896
19°	1.70239	1.70723	1.71207	1.71691	1.72175	1.72659	1.73143	1.73627	1.74111	1.74595	1.75078	1.75562	1.76046
20°	1.69412	1.69894	1.70377	1.70859	1.71341	1.71823	1.72305	1.72788	1.73270	1.73725	1.74234	1.74716	1.75199
21°	1.68571	1.69051	1.69532	1.70012	1.70493	1.70974	1.71454	1.71935	1.72415	1.72896	1.73377	1.73857	1.74338
22°	1.67722	1.68201	1.68680	1.69151	1.69638	1.70117	1.70596	1.71075	1.71554	1.72033	1.72512	1.72991	1.73470
23°	1.66862	1.67340	1.67817	1.68294	1.68772	1.69249	1.69727	1.70204	1.70681	1.71159	1.71636	1.72114	1.72591
24°	1.65994	1.66470	1.66945	1.67421	1.67897	1.68372	1.68848	1.69324	1.69799	1.70275	1.70751	1.71227	1.71702
25°	1.65113	1.65587	1.66061	1.66535	1.67009	1.67484	1.67958	1.68432	1.68906	1.69380	1.69854	1.70329	1.70803
	720	722	724	726	728	730	732	734	736	738	740	742	744

MILLIMETRES.

CENTIMETRE OF CARBONIC ACID

of mercury, and from 10° *to* 25° *Cent.*

MILLIMETRES.

746	748	750	752	754	756	758	760	762	764	766	768	770	TEMPERATURE CENT.
1.83936	1.84435	1.84934	1.85433	1.85933	1.86432	1.86931	1.87430	1.87930	1.88429	1.88928	1.89427	1.89926	10°
1.83134	1.83631	1.84129	1.84626	1.85123	1.85621	1.86118	1.86616	1.87113	1.87610	1.88108	1.88605	1.89103	11°
1.82324	1.82820	1.83315	1.83811	1.84307	1.84802	1.85298	1.85793	1.86289	1.86785	1.87280	1.87776	1.88271	12°
1.81521	1.82015	1.82510	1.83004	1.83499	1.83993	1.84488	1.84982	1.85477	1.85971	1.86466	1.86960	1.87455	13°
1.80714	1.81208	1.81701	1.82194	1.82687	1.83181	1.83674	1.84167	1.84661	1.85154	1.85647	1.86141	1.86634	14°
1.79880	1.80371	1.80861	1.81352	1.81843	1.82333	1.82824	1.83314	1.83805	1.84296	1.84786	1.85277	1.85767	15°
1.79056	1.79545	1.80034	1.80523	1.81012	1.81501	1.81990	1.82479	1.82968	1.83457	1.83946	1.84435	1.84924	16°
1.78216	1.78703	1.79189	1.79676	1.80163	1.80650	1.81136	1.81623	1.82110	1.82596	1.83083	1.83570	1.84056	17°
1.77381	1.77867	1.78353	1.78838	1.79324	1.79809	1.80295	1.80781	1.81266	1.81752	1.82237	1.82723	1.83209	18°
1.76530	1.77014	1.77498	1.77982	1.78466	1.78950	1.79434	1.79917	1.80401	1.80885	1.81369	1.81853	1.82337	19°
1.75631	1.76113	1.76645	1.77127	1.77610	1.78092	1.78574	1.79056	1.79538	1.80021	1.80503	1.80985	1.81467	20°
1.74818	1.75299	1.75780	1.76260	1.76741	1.77221	1.77702	1.78183	1.78663	1.79144	1.79624	1.80105	1.80586	21°
1.73949	1.74428	1.74907	1.75386	1.75865	1.76344	1.76823	1.77302	1.77781	1.78260	1.78739	1.79218	1.79697	22°
1.73068	1.73546	1.74023	1.74501	1.74978	1.75455	1.75933	1.76410	1.76888	1.77365	1.77842	1.78320	1.78797	23°
1.72178	1.72654	1.73129	1.73605	1.74081	1.74556	1.75032	1.75508	1.75984	1.76459	1.76935	1.77411	1.77886	24°
1.71277	1.71751	1.72225	1.72699	1.73173	1.73648	1.74122	1.74596	1.75070	1.75544	1.76018	1.76492	1.76967	25°
746	748	750	752	754	756	758	760	762	764	766	768	770	

MILLIMETRES.

time. The tube *h* can also be used repeatedly without being refilled. The second time it is employed connect it, for the sake of precaution, with a separately weighed tube of the small kind. The latter rarely increases in weight, and the first tube can, therefore, be then used a third time. If after this the second tube has become heavier, at the fourth operation reject the first tube, and use the second tube alone, and so on.

When large quantities of carbonic acid are to be absorbed, the tube *g* may be replaced with advantage by a LIEBIG's potash apparatus.

f. Separation from all Bases without exception (Estimation of the Acid by Expulsion, Absorption, and Volumetric Analysis).

It is sometimes advantageous, especially in the estimation of very small quantities of carbonic acid, to receive the same in a known volume of standard lime- or baryta-water, and to complete the analysis according to PETTENKOFER's principle (I., *b*, β).

g. Estimation by Measuring the Gas.

This process is applicable in the case of all salts which are decomposed by hydrochloric acid in the cold. It is distinguished for rapid and convenient execution and very satisfactory results. [The azotometer, fig. 58, is employed, and the details of the process are for the most part similar to those followed in the estimation of ammonia as described on page 159. The weighed carbonate is put in the bottle *a*, and the tube *f* is charged

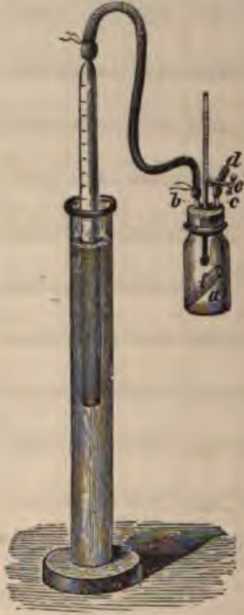

Fig. 58

with 5 c.c. of H. Cl., sp. gr. 1·125. When the burette is adjusted to zero, the acid is poured *at once* upon the carbonate. The precautions to be observed in the measurement of the gas are as detailed on page 161. It is not needful to wait so long for the gas to cool. The necessary corrections are applied by aid of the foregoing tables given by Dietrich,* pp. 295–6–7. Their use is perfectly similar to that of the tables given on pages 160 and 162–3.]

§ 140.

2. Silicic Acid.

I. *Determination.*

The direct estimation of silicic acid is invariably effected by converting the soluble modification of the acid into the insoluble modification, by evaporating and completely drying; the insoluble modification is then, after removal of all foreign matter, ignited and weighed.

For the guidance of the student I would observe here that, to guard against mistakes, he should always *test the purity of the weighed silicic acid.* The methods of testing will be found below.

If you have free silicic acid in the state of hydrate, in an aqueous or acid solution free from other fixed bodies, simply evaporate the solution in a platinum dish, ignite and weigh the residue.

II. *Separation of Silicic Acid from the Bases.*

a. In all compounds which are decomposed by Hydrochloric or Nitric Acid, on digestion in open vessels.

To this class belong the silicates soluble in water, as well as many of the insoluble silicates, as, for instance, nearly all zeolites.

The compound under examination is very finely pulverized, the powder dried at 100° (not above), and put into a platinum or porcelain dish (in the case of silicates whose solution might be attended with disengagement of chlorine, platinum cannot be used); a little water is then added, and the powder mixed to a uniform paste. Moderately concentrated hydrochloric acid, or—if the substance contains lead or silver—nitric acid, is now added, and the mixture digested at a very gentle heat, with constant stirring, until the substance is completely decomposed, in other terms until the glass rod, which is rounded at the end, encounters no more gritty powder, and the stirring proceeds smoothly without the least grating.

The silicates of this class do not all comport themselves in the same manner in this process, but show some differences; thus most of them form a bulky gelatinous mass, whilst in the case of others the silicic acid separates as a light pulverulent precipitate; again, many of them are decomposed readily and rapidly, whilst others require protracted digestion.

When the decomposition is effected, the mixture is evaporated to dryness on the water-bath, and the residue heated, with frequent stirring, until all the small lumps have crumbled to pieces, and the whole mass is thoroughly dry, and until no more acid fumes escape. It is always the *safest* way to conduct the operation of drying on the water-bath. Occasionally it is well to moisten the dry mass with water and evaporate again.

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* Fres. Zeitschrift, iv., 11, 142–145.

In cases where it appears desirable to accelerate the desiccation by the application of a stronger heat, as when deliquescent chlorides are present, an air-bath may be had recourse to; which may be constructed in a simple way, by suspending the dish containing the substance, with the aid of wire, in a somewhat larger dish of silver or iron, in a manner to leave everywhere between the two dishes a small space of uniform width. Direct heating over the lamp is not advisable, as in the most strongly heated parts the silicic acid is liable to unite again with the separated bases to compounds which are not decomposed, or only imperfectly, by hydrochloric acid.

When the mass is cold, it is brought to a state of semi-fluidity by thoroughly moistening it with hydrochloric acid; after which it is allowed to stand for half an hour, then warmed on a water-bath, diluted with hot water, stirred, allowed to deposit, and the fluid decanted on to a filter; the residuary silicic acid is again stirred with hot water, and the fluid once more decanted; after a third repetition of the same operation, the precipitate also is transferred to the filter, thoroughly washed with hot water, well dried, and ignited at last as strongly as possible, as directed in § 52 or in § 53. For the properties of the residue, see § 93, 9. The results are accurate. The bases, which are in the filtrate as chlorides, are determined by the methods given above. Deviations from the instructions here given are likely to entail loss of substance; thus, for instance, if the mass is not *thoroughly* dried, a not inconsiderable portion of the silicic acid passes into the solution, whereas if the instructions are strictly complied with, only traces of the acid are dissolved; in accurate analyses, however, even such minute traces must not be neglected, but should be separated from the bases precipitated from the solution. This separation may be readily effected by dissolving them, after ignition and weighing, in hydrochloric or sulphuric acid, by long digestion in the heat; the minute portion of silicic acid is left undissolved. Again, if the silicic acid is not *thoroughly* dried previous to ignition, the aqueous vapor disengaged upon the rapid application of a strong heat may carry away particles of the light and loose silica.

The *purity* of the silicic acid* may be conveniently tested in the following manner:—Heat a moderately concentrated solution of pure carbonate of soda to boiling, in a silver or platinum dish, or in a porcelain dish, and add a small quantity of the silicic acid. If it dissolves completely, this is a proof of its purity; but if it leaves a residue, the remainder of the silicic acid must be weighed, and the amount of impurity determined as directed in *b*, and the result, of course, calculated to the whole amount of the silica.

If you have pure hydrofluoric acid, you may also test the purity of the silicic acid in a very easy manner, by treating it with this acid and some sulphuric acid in a platinum dish; upon the evaporation of the solution, the silicic acid, if *pure*, will volatilize completely (as fluoride of silicon). If a residue remains, moisten this once more with hydrofluoric acid, add a few drops of sulphuric acid, evaporate, and ignite; the residue consists of the sulphates of the bases which were mixed with the silicic acid, as well as any titanic acid that was present (BERZELIUS).

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* This testing is more especially necessary in cases where the silicic acid has separated, not in the gelatinous state, but in the pulverulent form.

b. Compounds which are not decomposed by Hydrochloric Acid or Nitric Acid, on digestion in open vessels.

a. Decomposition by Fusion with Alkaline Carbonate.

Reduce the substance to an impalpable powder, by trituration and sifting (§ 25); transfer to a platinum crucible, and mix with about 4 times the weight of pure anhydrous carbonate of soda, with the aid of a rounded glass rod; wipe the rod against a small portion of the carbonate of soda on a card, and transfer this also from the card to the crucible. Cover the latter well, and heat, according to size, over a gas- or spirit-lamp with double draught, or a blast gas-lamp; or insert in a Hessian crucible, compactly filled up with calcined magnesia, and heat in a charcoal fire.

Apply at first a moderate heat for some time to make the mass simply agglutinate; the carbonic acid will, in that case, escape from the porous mass with ease and unattended with spirting. Increase the heat afterwards, finally to a very high degree, and terminate the operation only when the mass appears in a state of calm fusion, and gives no more bubbles.

The platinum crucible in which the fusion is conducted must not be too small; in fact, the mixture should only half fill it. The larger the crucible, the less risk of loss of substance. As it is of importance to watch the progress of the operation, the lid must be easily removable; a concave cover, simply lying on the top, is therefore preferable to an overlapping lid. In heating over a lamp, the crucible should always be supported on a triangle of platinum wire (see fig. 40, p. 64), with the opening just sufficiently wide to allow the crucible to drop into it fully one-third, yet to retain it firmly, even with the wire at an intense red heat. When conducting the process over a simple gas-lamp, it is advisable, towards the end of the operation, when the heat is to be raised to the highest degree, to put a chimney over the crucible, with the lower border resting on the ends of the iron triangle which supports the platinum triangle; this chimney should be about 12 or 14 cm. high, and the upper opening measure about 4 cm. in diameter.

When the fusion is ended, the red-hot crucible is removed with tongs, and placed on a cold, thick, clean iron plate, on which it will rapidly cool; it is then generally easy to detach the fused cake in one piece.

The cake (or the crucible with its contents) is put into a beaker, from 10 to 15 times the quantity of water poured over it, and hydrochloric acid gradually added, or, under certain circumstances, nitric acid; the beaker is kept covered with a large watch-glass or porcelain dish, perfectly clean outside, to prevent the loss of the drops of fluid which the escaping carbonic acid carries along with it; the drops thus intercepted by the cover are afterwards rinsed into the beaker. The crucible is also rinsed with dilute acid, and the solution obtained added to the fluid in the beaker.

The solution is promoted by the application of a gentle heat, which is continued for some time, to insure the expulsion of the carbonic acid; since otherwise some loss of substance might be incurred, in the subsequent evaporation, by spirting.

If in treating the fused mass with hydrochloric acid, a powder subsides (chloride of sodium or chloride of potassium), more water is required.

If the decomposition of the mineral has succeeded, the hydrochloric solution is either perfectly clear, or light flakes of silicic acid only float in it. But if a heavy powder subsides, which feels gritty under the glass rod, this consists of undecomposed mineral. The cause of such imperfect decomposition is generally to be ascribed to imperfect pulverization.

In such cases the undecomposed portion may be fused once more with carbonated alkali; the better way, however, is to repeat the process with a fresh portion of mineral more finely pulverized.

The hydrochloric or nitric solution is poured, together with the precipitate of silicic acid, into a porcelain, or, better, into a platinum dish, and treated as directed in II., *a*.

That the fluid may not be too much diluted, the beaker should be rinsed only once, or not at all, and the few remaining drops of solution dried in it; the trifling residue thus obtained is treated in the same way as the residue left in the evaporating basin.

This is the method most commonly employed to effect the decomposition of silicates that are undecomposable by acids; that it cannot be used to determine alkalies in silicates is evident.

β. *Decomposition by means of Hydrofluoric Acid.*

The finely-pulverized silicate is mixed, in a platinum dish, with rather concentrated, slightly fuming hydrofluoric acid, the acid being added gradually, and the mixture stirred with a thick platinum wire. The mixture, which has the consistence of a thin paste, is digested some time on a water-bath at a gentle heat, and pure concentrated sulphuric acid, diluted with an equal quantity of water, is then added, drop by drop, in more than sufficient quantity to convert all the bases present into sulphates. The mixture is evaporated on the water-bath to dryness, during which operation fluoride of silicon gas and hydrofluoric acid gas are continually volatilizing; it is finally exposed to a stronger heat at some height above the lamp, until the excess of sulphuric acid is almost completely expelled. The mass, when cold, is thoroughly moistened with concentrated hydrochloric acid, and allowed to stand for one hour; water is then added, and a gentle heat applied. If the decomposition has fully succeeded, the whole must dissolve to a clear fluid. If an undissolved residue is left, the mixture is heated for some time on the water-bath, then allowed to deposit, the clear supernatant fluid decanted as far as practicable, the residue dried, and then treated again with hydrofluoric acid and sulphuric acid, and, lastly, with hydrochloric acid, which will now effect complete solution, provided the analyzed substance was very finely pulverized, and free from baryta, strontia (and lead). The solution is added to the first. The bases in the solution (which contains them as sulphates, and contains also free hydrochloric acid) are determined by the methods which will be found in Section V.

The hydrofluoric acid may also be employed in combination with hydrochloric acid; thus 1 grm. of finely elutriated felspar, mixed with 40 c. c. water, 7 c. c. hydrochloric acid of $25\frac{0}{0}$ and $3\frac{1}{2}$ c. c. hydrofluoric acid, and heated to near the boiling point, dissolves completely in three minutes. 4 c. c. sulphuric acid are then added, the sulphate of baryta which separates is filtered off, and the filtrate evaporated till no more hydrofluoric acid escapes (AL. MITSCHERLICH *).

The execution of the method requires the greatest possible care, both the liquid and the gaseous hydrofluoric acid being most injurious substances. The treatment of the silicate with the acid and the evaporation must be conducted in the open air, otherwise the windows and all glass apparatus will be attacked. As the silicic acid is in this method simply inferred from the loss, a combination with the method *α* is often resorted to. [See also § 160, **85.**]

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* Journ. f. prakt. Chem. 81, 108.

[*γ. Decomposition by ignition with Carbonate of Lime and Chloride of Ammonium.* PROF. J. L. SMITH'S METHOD for separating alkalies.

Mix 1 part of the pulverized silicate with 1 part of dry chloride of ammonium,* by gentle trituration in a smooth mortar, then add 8 parts of carbonate of lime (Qual. Anal. p. 83) and mix intimately. Bring the mixture into a platinum crucible, rinsing the mortar with a little carbonate of lime. Warm the crucible gradually over a small Bunsen burner until fumes of ammonia-salts no longer appear, then heat to full redness, but not too intensely, for from 30 to 40 minutes.† The mass should sinter together, but not fuse. When cold it may be usually detached with ease from the crucible. It is heated to boiling in a capsule with 100 c. c. of water for several hours, or until it is entirely disintegrated and no lumps remain. Should the mass, from overheating, remain partially coherent after long boiling, it may be transferred to a porcelain mortar and ground finely, and then boiled as before. Certain silicates, *e. g.* those containing much protoxide of iron, fuse easily with the proportions of flux above given. In their case it is better to repeat the ignition on a new portion, using 10 or 12 parts of carbonate of lime and bringing only the lower three-fourths of the crucible to a red heat.

The fluxed mass, when completely disintegrated by boiling with water, yields to this solvent all the alkalies, with some chloride of calcium and caustic lime. It is filtered and well washed. To the liquid is added carbonate of ammonia (1—2 grms.) in solution, and the whole is evaporated to a bulk of about 30 c. c. Then a little more carbonate of ammonia, with some caustic ammonia, is added, to insure complete separation of the lime. Filter and collect the filtrate and washings in a weighed platinum capsule, evaporate to dryness on the water-bath, dry further, supporting the capsule within an iron cup to which heat is applied, and finally heat carefully almost to redness, to expel ammonia-salts. When cool, weigh. The alkali-chlorides thus obtained are nearly pure; but on dissolving in a few drops of water, a little black residue is usually seen. This may be removed, if weighable, by filtration, using a very small filter. Prof. SMITH'S method is by far the most convenient and accurate for separating alkalies from a silicate, and is universally applicable, except, perhaps, in presence of boracic acid.]

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* The chloride of ammonium is best obtained in a pulverulent condition by dissolving some of the salt in hot water and evaporating rapidly; the greater portion of the chloride of ammonium will deposit itself in a pulverulent condition, the water is poured off, and the salt thrown on bibulous paper, allowed to dry; the final desiccation being carried on in a water-bath, or in any other way with a corresponding temperature.

† An ordinary portable furnace, with a conical sheet-iron cap, of from two to three feet high, likewise answers the purpose perfectly well, all the requisite heat being afforded by it.

SECOND GROUP.

HYDROCHLORIC ACID—HYDROBROMIC ACID—HYDRIODIC ACID—HYDROCYANIC ACID—HYDROSULPHURIC ACID.

§ 141.

1. HYDROCHLORIC ACID.

I. *Determination.*

Hydrochloric acid may be determined very accurately in the gravimetric as well as in the volumetric way.*

a. Gravimetric Method.

Determination as Chloride of Silver.

Solution of nitrate of silver, mixed with some nitric acid, is added in excess to the solution under examination, the precipitated chloride is made to unite by application of heat and shaking, washed by decantation, dried, and ignited. The details of the process have been given in § 115, 1, *a*, α. Care must be taken not to heat the solution mixed with nitric acid, before the solution of nitrate of silver has been added in excess. As soon as the latter is present in excess, the chloride of silver separates immediately and completely upon shaking the vessel, and the supernatant fluid becomes perfectly clear after standing a short time in a warm place. The determination of hydrochloric acid by means of silver is therefore more readily effected than that of silver by means of hydrochloric acid. In the case of smaller quantities of chloride of silver, the precipitate is often collected on a filter; see § 115, 1, *a*, β. Or the two methods may be combined in this way—that the chief portion of the precipitate is washed by decantation, dried in the porcelain crucible, and ignited, the decanted fluid being passed through a filter, to make quite sure that not a particle of chloride of silver be lost. The filter is, after drying, incinerated on the inverted cover of the porcelain crucible, the ashes are treated with a few drops of nitric acid, some hydrochloric acid is added, the mixture evaporated to dryness, the residue gently ignited, and the lid replaced on the crucible in which the chloride has been heated to incipient fusion; a gentle heat is then once more applied, after which the crucible is allowed to cool under the desiccator, and then weighed.

b. Volumetric Methods.

α. By Solution of Nitrate of Silver.

This convenient and accurate method requires a perfectly neutral solution of nitrate of silver of known value. [This is best prepared by weighing off in a porcelain crucible about 4·8 grm. of clean crystallized nitrate of silver, fusing it at the lowest possible heat, and then ascertaining its weight accurately. After fusion it should weigh *a little more* than 4·7933 grm., the quantity that, contained in a litre of water, gives a solution of which 1 c. c. =·001 grm. of chlorine. The fused salt is dissolved in a little warm water, the solution brought into a litre flask and filled to the mark, observing the usual precautions as to temperature, &c. When thus adjusted, add to the contents of the flask, from a burette, enough water to bring the excess of nitrate of silver above 4·7933 grms. to the requisite dilution.

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* For the acidimetric estimation of free hydrochloric acid, see § 204.

grm. c. c. grm. c. c.
4·7933 : 1000 :: Excess over 4·7933 : Excess over 1000.

In this way it is easy with a burette and a litre flask to make a perfectly accurate standard solution, while this would be hardly possible should the operator weigh off *less* than 4·7933 grm. of nitrate of silver.

This solution, which may be preserved in a well-corked bottle indefinitely, without change, is next tested by means of pure chloride of sodium. Either an equivalent solution is made by dissolving 1·6486 grm. of the coarsely powdered and gently ignited salt in 1 litre of water, and portions of 20 c. c. are taken, or several portions of the dry salt, 0·05 grm., are weighed off and dissolved, each in a separate beaker, in 20—30 c. c. of water. To each solution 2 drops of a cold saturated solution of pure yellow chromate of potassa is added.]

Fill a Mohr's burette (if it has an Erdmann's float so much the better) up to zero with the silver solution, and allow to drop slowly, with constant stirring, into the light yellow solution contained in one of the beakers. Each drop produces, where it falls, a red spot, which on stirring disappears, owing to the instant decomposition of the chromate of silver with the chloride of sodium. At last, however, the slight red coloration remains. Now all chlorine has combined with silver, and a little chromate of silver has been permanently formed. [The number of c. c. of silver solution should be equal to the number of milligrammes of chlorine in the Na Cl employed. An excess of about 0·2 c. c. of silver solution will be required to produce a visible coloration, and hence this quantity may be deducted from the amount used. Should repeated trials show that the silver solution is not of exactly the intended strength, it may be brought to the precise standard by addition of water or nitrate in requisite quantity. It is, however, ordinarily better to take the mean of several accordant determinations of the quantity of chlorine precipitated by 1 c. c. of the silver solution, and write this number on the label of the bottle, to be employed as a factor into which the no. of c. c. of silver solution required in any analysis is to be multiplied to find the quantity of chlorine sought for.]

Being now in possession of a standard silver solution, and being practised in exactly hitting the transition from yellow to the shade of red, we can determine with precision hydrochloric acid or chlorine in the form of a metallic chloride soluble in water. The fluid to be tested must be neutral—free acids dissolve the chromate of silver. The solution of the substance is therefore, if necessary, rendered neutral by addition of nitric acid or carbonate of soda (it should be rather alkaline than acid), about 2 drops of the solution of yellow chromate added, and then silver from the burette, till the reddish coloration is just perceptible.

If the operator fears he has added too much silver solution, *i.e.*, if the red color is too strongly marked, he may add 1 c. c. of a solution of chloride of sodium containing 1·6486 in a litre (and therefore corresponding to the silver solution), and then add the silver drop by drop again. Of course in this case 1 c. c. must be deducted from the amount of silver solution used.

The results are very satisfactory.

The fluid to be analysed should be about the same volume as the solutions employed in standardizing the silver solution, and also about the same strength, otherwise the small quantity of silver which produces the coloration will not stand in the same proportion to the chlorine present. This small quantity of silver solution is extremely small, about 0·20 c. c., the inaccuracy hereby arising even in the case of quantities of chlorine differing widely from that originally used in standardizing the silver solution is therefore almost inconsiderable. If the amount of silver solution necessary to impart the coloration always remained the same, we should have simply to deduct the amount in question with all experiments in order to avoid this small inaccuracy entirely; since, however, this is not the case, but, on the contrary, much chloride of silver requires somewhat more chromate of silver for visible coloration, than less chloride of silver, this method of proceeding would not always increase the exactness of the results.

β. *By Solution of Nitrate of Silver and Iodide of Starch* (PISANI's method*).

Add to the solution of the chloride, acidified with nitric acid, a slight excess of solution of nitrate of silver of known strength, warm, and filter. Determine the excess of silver in the filtrate by means of solution of iodide of starch (see p. 215), and deduct this from the amount of silver solution used. The difference shows the quantity of silver which has combined with the chlorine; calculate from this the amount of the latter. Results satisfactory.

Of these volumetric methods of estimating chlorine, the first deserves the preference in all ordinary cases. PISANI's method (*b*, β) is especially suited for the estimation of very minute quantities of chlorine, but is not applicable when—as in nitre analyses—large quantities of alkaline nitrate are present (p. 211).

II. *Separation of Chlorine from the Metals.*

a. In Soluble Chlorides.

The same method as in I., *a*. The metals in the filtrate are separated from the excess of the salt of silver by the methods which will be found in Section V.

Bichloride of tin, *chloride of mercury*, the *chlorides of antimony*, and the *green chloride of chromium*, form exceptions from the rule.

α. From solution of *bichloride of tin*, nitrate of silver would precipitate, besides chloride of silver, a compound of binoxide of tin and oxide of silver. To precipitate the tin, therefore, the solution is mixed with a concentrated solution of nitrate of ammonia, allowed to deposit, the fluid decanted, and filtered (compare § 126, 1, *b*), and the chlorine in the filtrate is precipitated with solution of silver. LÖWENTHAL, the inventor of this method, has proved its accuracy.†

β. When a solution of *chloride of mercury* is precipitated with solution of nitrate of silver, the chloride of silver thrown down contains an admixture of mercury. The mercury is, therefore, first precipitated by sulphuretted hydrogen, which must be added in sufficient excess, and the chlorine in the filtrate determined as directed in § 169.

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* Annal. d. Mines, X. 83; Liebig and Kopp's Jahresbericht f. 1856, 751.

† Journ. f. prakt. Chem, 56, 371.

γ. *The chlorides of antimony* are also decomposed in the manner described in β. The separation of basic salt upon the addition of water may be avoided by addition of tartaric acid. The sulphide of antimony should be tested for chlorine.

δ. Solution of silver fails to precipitate the whole of the chlorine from solution of the *green chloride of chromium* (PÉLIGOT). The chromium is, therefore, first precipitated with ammonia, the fluid filtered, and the chlorine in the filtrate precipitated as directed in I., *a.*

b. In Insoluble Chlorides.

α. Chlorides soluble in Nitric Acid.

Dissolve the chloride in nitric acid, without applying heat, and proceed as directed in I., *a.*

β. *Chlorides insoluble in Nitric Acid* (chloride of lead, chloride of silver, subchloride of mercury).

aa. Chloride of lead is decomposed by digestion with alkaline bicarbonate and water. The process is exactly the same as for the decomposition of sulphate of lead (§ 132. II., *b.*, β).

bb. Chloride of silver is ignited in a porcelain crucible, with 3 parts of carbonate of soda and potassa, until the mass commences to agglutinate. Upon treating the mass with water, the metallic silver is left undissolved; the solution contains the alkaline chloride, which is then treated as directed in I., *a.*

Chloride of silver may also be readily decomposed by digestion with pure zinc, and dilute sulphuric acid. The separated metallic silver may be weighed as such; it must afterwards be ascertained, however, whether it dissolves in nitric acid to a clear fluid. The chlorine is determined in the solution of chloride of zinc obtained, as in I., *a.*

cc. Subchloride of mercury is decomposed by digestion with solution of soda or potassa. The hydrochloric acid in the filtrate is determined as in I., *a.* The suboxide of mercury is dissolved in nitric or nitrohydrochloric acid, and the mercury determined as directed in § 117 or § 118.

c. The soluble chlorides of the metals of the fourth, fifth, and sixth groups may generally be decomposed also by sulphuretted hydrogen, or, as the case may be, sulphide of ammonium. The hydrochloric acid in the filtrate is determined as directed in § 169. It must not be omitted to test the precipitated sulphides for chlorine.

d. In many metallic chlorides, for instance, in those of the first and second groups, the chlorine may be determined also by evaporating with sulphuric acid, converting the base thus into a sulphate, which is then ignited and weighed as such; the chlorine being calculated from the loss. This method is not applicable in the case of chloride of silver and chloride of lead, which are only imperfectly and with difficulty decomposed by sulphuric acid; nor in the case of chloride of mercury and bichloride of tin, which sulphuric acid fails almost or altogether to decompose.

Supplement.

Determination of Chlorine in the Free State.

§ 142.

Chlorine in the free state may be determined both in the volumetric and in the gravimetric way. The volumetric methods, however, deserve the preference in most cases. They are very numerous.

I shall only here adduce that one which is undoubtedly the most accurate and at the same time the most convenient.*

1. *Volumetric Method.*

With Iodide of Potassium (*after* BUNSEN).

Bring the chlorine, in the gaseous form or in aqueous solution, into contact with an excess of solution of iodide of potassium in water. Each eq. chlorine liberates 1 eq. iodine. By determining the liberated iodine by means of hyposulphite of soda as described in § 146, you will learn the quantity of chlorine with the greatest accuracy. If you have to determine the chlorine of chlorine water, measure a portion off with a pipette. To prevent any of the gas entering the mouth, connect the upper end of the pipette with a tube containing moist hydrate of potassa laid between cotton. When the pipette has been correctly filled allow its contents to flow, with stirring, into an excess of solution of iodide of potassium (1 in 10). When the latter is in excess, a black precipitate is formed. If the chlorine is evolved in the gaseous condition, you may employ either the apparatus given in § 130, I., *d*, *β*, or the following, which is especially suitable where the chlorine is not pure, but is mixed with other gases.

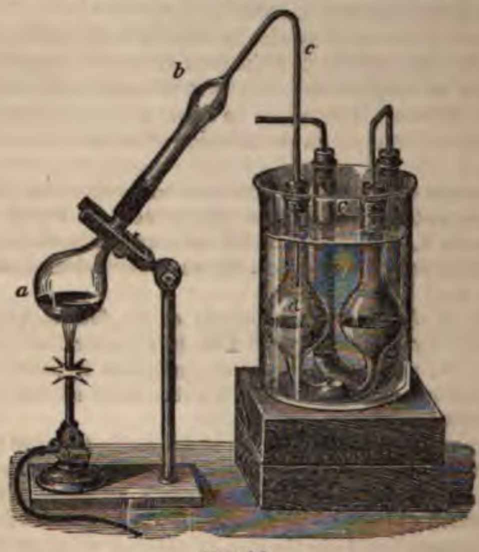

Fig. 59.

a is a little flask, from which the chlorine is evolved by boiling the substance with hydrochloric acid; it is connected with the tube *b* by means of a flexible tube. The latter must be free from sulphur—should it contain sulphur it is well boiled with dilute potassa and then thoroughly washed. The thinner tube *c*, which has been fused to the bulb of *b*, leads through the caoutchouc stopper (which has been deprived of sulphur) to the bulbed U-tube *d*, which contains solution of iodide of potassium, and which for safety is connected with the plain U-tube *e*, also containing iodide of potassium solution. Both tubes stand in a beaker filled with water. The apparatus offers the advantages that the fluid cannot return, that the iodide of potassium remains cold, and that the absorption is complete. After all the chlorine has been expelled by boiling long enough, rinse *d* and *e* out into a beaker and measure the iodine with standard hyposulphite of soda (§ 146).

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* Compare article "Chlorimetry" in the Special Part.

2. *Gravimetric Method.*

The fluid under examination, which must be free from sulphuric acid, say, for instance, 30 grm. chlorine water, is mixed in a stoppered bottle, with a slight excess of hyposulphite of soda, say 0·5 grm., the stopper inserted, and the bottle kept for a short time in a warm place; after which the odor of chlorine has disappeared. The mixture is then heated to boiling with some hydrochloric acid in excess, to destroy the excess of hyposulphite of soda, filtered, and the sulphuric acid in the filtrate determined by baryta (§ 132). 1 eq. sulphuric acid corresponds to 2 eq. chlorine (WICKE[*]).

In fluids containing, besides free chlorine, also hydrochloric acid, or a metallic chloride, the chlorine existing in a state of combination may be determined, in presence of the free chlorine, in the following way:—

A weighed portion of the fluid is mixed with solution of sulphurous acid in excess, the mixture acidified, after some time, with nitric acid, and the whole of the chlorine precipitated as chloride of silver. The quantity of the free chlorine is then determined in another weighed portion, by means of iodide of potassium; the difference gives the amount of combined chlorine.[†]

Having thus seen in how simple and accurate a manner the quantity of free chlorine may be determined by BUNSEN's method, it will be readily understood that all oxides and peroxides which yield chlorine when heated with hydrochloric acid, may be analyzed by heating them with concentrated hydrochloric acid, and determining the amount of chlorine evolved. For the *modus operandi* compare 1.

§ 143.

2. HYDROBROMIC ACID.

I. *Determination.*

a. As bromide of silver. Free hydrobromic acid—in a solution free from hydrochloric acid or chlorides—is precipitated by silver solution, and the further process is conducted as in the case of hydrochloric acid (§ 141). For the properties of bromide of silver, see § 94, 2. The results are perfectly accurate.

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[*] Annal. d. Chem. u. Pharm. 99, 99.

[†] If chlorine water is mixed at once with solution of nitrate of silver, $\frac{5}{6}$ only of the chlorine are obtained as chloride of silver: $6\,Cl + 6\,Ag\,O = 5\,Ag\,Cl + Ag\,O, Cl\,O_5$ (H. Rose, Weltzien, Annal. d. Chem. u. Pharm. 91, 45). If chlorine water is mixed with ammonia in excess, there are formed at first chloride of ammonium and hypochlorite of ammonia, the latter then gradually decomposes into nitrogen and chloride of ammonium; however, a little chlorate of ammonia is also formed besides (Schönbein, Journ. f. prakt. Chem. 84, 386); Zeitschrift f. analyt. Chem. 2, 59.

The following methods are especially serviceable for the determination of small amounts of bromine; they are applicable in the presence of chlorides.

b. With chlorine water and chloroform (*after* A. REIMANN*). This method depends on the facts that chlorine when added to bromides first liberates the bromine and then combines with it, and that bromine colors chloroform yellow or orange, while chloride of bromine merely communicates a yellowish tinge to that fluid. The process is as follows:—Mix the liquid containing a bromide of an alkali metal in neutral solution, in a stoppered bottle with a drop of pure chloroform about the size of a hazel-nut, then add standard chlorine water from a burette, protected from the light by being surrounded with black paper. On shaking, the chloroform becomes yellow, on further addition of chlorine water, orange, then yellow again, and lastly—at the moment when 2 eq. chlorine have been used for 1 eq. bromine—yellowish white ($K\,Br + 2\,Cl = K\,Cl + Br\,Cl$). Considerable practice and skill are required before the operator can tell the end-reaction. He will be assisted by placing the bottle on white paper and comparing the color of the chloroform with that of a dilute solution of yellow chromate of potassa of the required color. The strength of the chlorine water should depend on the amount of the bromine to be determined. It should be so adjusted that about 100 c. c. may be used. The chlorine water is standardized with iodide of potassium and hyposulphite of soda (§ 142, 1). The method is especially suited for the determination of small quantities of bromine in mother liquors, kelp, &c. The results are very approximate: *e.g.*, 0·0180 instead of 0·0185—0·055 instead of 0·059—0·0112 instead of 0·0100, &c. If the fluid contains organic substances, it is—after being rendered alkaline with caustic soda—evaporated to dryness, the residue ignited in a silver dish, extracted with water, the solution neutralized exactly with hydrochloric acid, and then tested.

c. HEINE's *colorimetric method.*† The bromine is liberated by means of chlorine, and received in ether; the solution is compared, with respect to color, with an ethereal solution of bromine of known strength, and the quantity of bromine in it thus ascertained. FEHLING‡ obtained satisfactory results by this method. It will at once be seen that the amount of bromine contained in the fluid to be analyzed must be known in some measure, before this method can be resorted to. As the brine examined by FEHLING could contain at the most 0·02 grm. bromine in 60 grm., he prepared ten different test fluids, by adding to ten several portions of 60 grm. each of a saturated solution of common salt increasing quantities of bromide of potassium, containing respectively from 0·002 grm. to 0·020 grm. bromine. He added an equal volume of ether to the test fluids, and then chlorine water, until there was no further change observed in the color of the ether. It being of the highest importance to hit this point exactly, since too little as well as too much chlorine makes the color appear lighter, FEHLING prepared three samples of each test fluid, and then chose the darkest of them for the comparison. 60 grm. are now taken§ of the mother liquor to be examined, the

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[*] Annal. d. Chem. u. Pharm. 115, 140.

[†] Journ. f. prakt. Chem. 36, 184, proposed to effect the determination of bromine in mother liquors.

[‡] Journ. f. prakt. Chem. 45, 269.

[§] The best way is to take them by measure.

same volume of ether added as was added to the test fluids, and then chlorine water. Every experiment is repeated several times. Direct sunlight must be avoided, and the operation conducted with proper expedition. In my opinion it is well to replace the ether by chloroform or bisulphide of carbon.

II. *Separation of Bromine from the Metals.*

The metallic bromides are analzyed exactly like the corresponding chlorides (§ 141, II., *a* to *d*), the whole of these methods being applicable to bromides as well as chlorides. In the decomposition of bromides by sulphuric acid (§ 141, II., *d*), porcelain crucibles must be used instead of platinum ones, as the latter would be attacked by the liberated bromine.

Supplement.

Determination of Free Bromine.

§ 144.

Free bromine in aqueous solution, or evolved in the gaseous form, is caused to act on excess of solution of iodide of potassium. Each eq. bromine liberates 1 eq. iodine, which is most conveniently determined by means of hyposulphite of soda (§ 146). As regards the best mode of bringing about the action of the bromine on the iodide of potassium, compare § 142, 1.

The determination of free bromine in presence of hydrobromic acid or metallic bromides is effected in the same manner as that of free chlorine in presence of hydrochloric acid (see § 142, at the end).

§ 145.

3. Hydriodic Acid.

I. *Determination.*

a. As Iodide of Silver, Gravimetrically.—If you have hydriodic acid in solution, free from hydrochloric and hydrobromic acids, precipitate with nitrate of silver, and proceed exactly as with hydrochloric acid (§ 141). For the properties of iodide of silver, see § 94, 3. The results are perfectly accurate.

b. As Protiodide of Palladium, Gravimetrically.—The following method, recommended first by Lassaigne, is resorted to exclusively to effect the separation of hydriodic acid from hydrochloric and hydrobromic acids, for which purpose it is extremely well adapted. Acidify the solution slightly with hydrochloric acid, and add a solution of protochloride of palladium, as long as a precipitate forms; let the mixture stand from 24 to 48 hours in a warm place, filter the brownish-black precipitate off on a weighed filter, wash with warm water, and dry at a temperature from about 70° to 80°, until the weight remains constant. The drying may be greatly facilitated by replacing the water (after the operation of washing) by some alcohol, and the latter fluid again by a little ether. For the properties of the precipitate, see § 94, 3. This method gives very accurate results, provided the drying be managed with proper care; but if the temperature is raised to near 100°, the precipitate smells of iodine, and a trifling loss is incurred.

Instead of simply drying the protiodide of palladium, and weighing it in that form, you may ignite it in a crucible of porcelain or platinum,* and calculate the iodine from the residuary metallic palladium (H. ROSE).

c. WITH CHLORINE WATER AND CHLOROFORM (after A. and F. DUPRÉ†). This is based upon the circumstance that, when chlorine water or solution of chloride of soda is added to a metallic iodide, the first equivalent of chlorine liberates iodine, which then combines with 5 more equivalents of chlorine to pentachloride of iodine. GOLFIER-BESSEYRE adds starch paste to render this transition perceptible, whilst A. and F. DUPRÉ employ, with much better success, chloroform or bisulphide of carbon, which are colored intensely violet by free iodine as well as by all compounds of iodine with chlorine containing less than 5 eq. chlorine.

The process may be conducted in two different ways.

α. Add chlorine water to a few litres of water, and determine the chlorine in the fluid as directed in § 142.

Take now of the fluid under examination a quantity containing no more than about 10 mgrm. iodine, and pour this into a stoppered bottle, add a few grammes of pure chloroform or pure bisulphide of carbon (free from sulphur and sulphuretted hydrogen), and then gradually, drop by drop, chlorine solution, adding and shaking vigorously by turns, until the violet color of the chloroform or bisulphide of carbon just disappears; which point may be hit with the greatest precision. 6 eq. chlorine consumed in this process correspond to 1 eq. iodine. A still simpler way is to determine the strength of the dilute chlorine water by making it act upon a known quantity of iodide of potassium, say 10 c. c. of a solution containing 0·001 grm. iodine in 1 c. c., and then to apply it to the fluid under examination. The amount of chlorine consumed in the first experiment is, in that case, to the known amount of iodine as the quantity consumed in the second experiment is to x.

In cases where the quantity of iodine is so considerable as, when separated, to impart a distinctly perceptible coloration to the fluid, it is better to delay adding the chloroform or bisulphide of carbon, until the color first produced has nearly disappeared again upon further addition of chlorine water.

That this method cannot be employed in presence of substances liable to be acted upon by free chlorine or iodine, is self-evident; organic matters, more particularly, must not be present. If they are, as is usually the case with mother liquors, the method *β* should be employed.

β. Add to the fluid under examination chloroform or bisulphide of carbon, then dilute chlorine water of unknown strength, until the fluid is *just* decolorized. At this point all the iodine is converted in $I\,Cl_5$. Add now solution of iodide of potassium in moderate excess; this will produce for every equivalent of $I\,Cl_5$, 6 eq. free iodine, which remain dissolved in the fluid. Determine the liberated iodine with hyposulphite of soda or sulphurous acid, as directed in § 146, and divide the quantity found by 6: the quotient expresses the quantity of iodine contained in the examined fluid.

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* This substance is not injured by the operation.

† Annal. d. Chem. u. Pharm. 94, 365.

In presence of bromides, Dupré's method requires certain modifications, for which I refer to § 169.

This method is suited more particularly for the estimation of minute quantities of iodine. The results are most accurate.

d. By Distillation with Sesquichloride of Iron (after Duflos). When hydriodic acid or a metallic iodide is heated, in a distillatory apparatus, with solution of pure sesquichloride of iron, the whole of the iodine escapes along with the aqueous vapor and protochloride of iron is formed ($Fe_2 Cl_3 + H I = 2 Fe Cl + H Cl + I$). The iodine passing over is received in solution of iodide of potassium (apparatus, fig. 59, p. 308), and its quantity determined by means of hyposulphite of soda or sulphurous acid, as directed § 146. In employing this method, it must be borne in mind that the sesquichloride of iron must be free from chlorine and nitric acid. It is best to prepare it from sesquioxide of iron and hydrochloric acid.

e. By Separation with Hyponitric Acid. See separation of iodine from chlorine, § 169.

II. *Separation of Iodine from the Metals.*

The metallic iodides are analyzed like the corresponding chlorides. From iodides of the alkali metals containing free alkali the iodine may be precipitated as iodide of silver, by first saturating the free alkali almost completely with nitric acid, then adding solution of nitrate of silver in excess, and finally nitric acid to strongly acid reaction. If an excess of acid were added at the beginning, free iodine might separate, which is not converted completely into iodide of silver by solution of nitrate of silver.

With respect to the salts insoluble in water, I have to observe that many of them are more advantageously decomposed by boiling with potassa or soda, than dissolved in dilute nitric acid, the latter process being apt to be attended with separation of iodine. This applies more particularly to subiodide of copper and to protiodide of palladium. From iodides soluble in water, the iodine may also be precipitated as protiodide of palladium.

Lastly, it is open to the analyst in almost all cases to determine the base in one portion of the compound, by heating with concentrated sulphuric acid, the iodine, in another portion, by the method I., *e.* The iodide of mercury is best decomposed by distillation with 8 to 10 parts of a mixture of 1 part cyanide of potassium with 2 parts anhydrous lime. Apparatus, fig. 50, p. 222; *a b* is filled with magnesite (H. Rose *).

Supplement.

Determination of Free Iodine.

§ 146.

The determination of free iodine is an operation of great importance in analytical chemistry, since, as Bunsen first pointed out, it is a means for the estimation of all those substances which, when brought into contact with iodide of potassium, separate from the same a definite quantity of iodine (*e.g.*, chlorine, bromine, &c.), or, when boiled with hydrochloric acid, yield a definite quantity of chlorine (*e.g.*, chromic acid, some peroxides, &c.). By causing the chlorine produced to act on iodide of potassium, we obtain the equivalent quantity of free iodine.

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* Zeitschrift f. anal. Chem. 2, 1.

BUNSEN AND SCHWARZ'S METHOD.

This method is based on the following reaction $2\ (NaO\ S_2\ O_2) + I = Na\ I + NaO\ S_4\ O_5$.

a. REQUISITES.

α. Iodine solution of known strengh. Dissolve 6·2 to 6·3 grm. iodine with the aid of about 9 grm. iodide of potassium (free from iodic acid) and water to about 1200 c. c.

β. Solution of *hyposulphite of soda.* Dissolve 12·2 to 12·3 grm. of the pure and dry salt in water to about 1200 c. c.

γ. Solution of *iodide of potassium.* Dissolve 1 part of the salt (free from iodic acid) in about 10 parts of water. The solution must be colorless and must remain so immediately after the addition of dilute sulphuric or hydrochloric acid (either must be iron-free).

δ. Starch solution. Stir the purest starch powder gradually with about 100 parts cold water and heat to boiling with constant stirring. Allow to cool quietly, and pour off the fluid from any deposit. The solution should be almost clear and free from all lumps. The starch solution is best prepared fresh before each series of experiments.

b. PRELIMINARY DETERMINATIONS.

α. Determination of the relation between the Iodine Solution and the Hyposulphite Solution.

Fill two burettes with the solutions. Run 20 c. c. of the hyposulphite into a beaker, add some water and 3 or 4 c. c. starch solution, then add the iodine till a blue coloration is just produced. If you have added a drop too much, run in one or two drops more of the hyposulphite, and then more cautiously one drop after another of the iodine solution. After a few minutes read off the height of the fluid in both burettes. Suppose we had used 20 c. c. hyposulphite to 20·2 c. c. iodine.

β. Exact Determination of the Iodine in the Solution.

This is performed by comparison with a known quantity of pure iodine; the process is, as far as my experience goes, best conducted in the following manner:—

Select three watch-glasses, *a*, *b*, and *c*, which fit each other; weigh *b* and *c* together accurately. Put about 0·5 grm. pure dry iodine (prepared according to § 65, 6) into *a*, place it on an iron plate and heat gently, till dense fumes of iodine escape. Now cover it with *b* and regulate the heat so that the iodine may sublime entirely or almost entirely into *b*. Next remove *b*, while still hot, give it a gentle swing in the air, to remove the still uncondensed iodine fumes and any traces of aqueous vapor, cover it with *c*, allow to cool under the desiccator, weigh and transfer the two watch-glasses, together with the weighed iodine, to a capacious beaker, containing a sufficient quantity of iodide of potassium solution to dissolve the whole of the iodine to a clear fluid. Now run in hyposulphite from the burette till the fluid is just decolorized, add 3 to 4 c. c. starch solution, and then iodine solution from a second burette, to incipient blueness.

After the two burettes have been read off, the following simple calculation gives the strength of the iodine solution :—

Suppose we had weighed off 0·150 grm. iodine, and used 29·5 c. c. hyposulphite and 0·3 c. c. iodine solution.

From α, we know that 20 c. c. hyposulphite correspond to 20·2 c. c. iodine solution; 29·5 c. c. therefore correspond to 29·8 c. c.

Now 29·5 c. c. hyposulphite correspond to 0·150 grm. iodine + 0·3 c. c. iodine solution.

But 29·5 c. c. hyposulphite also correspond to 29·8 c. c. iodine solution.

∴ 0·150 grm. iodine + 0·3 c. c. iodine solution = 29·8 c. c. iodine solution.

∴ 0·150 grm. iodine = 29·5 c. c. iodine solution.

∴ 1 c. c. iodine solution = 0·0050847 grm. iodine.

The experiment just described is repeated and the mean of the two results taken, provided they exhibit sufficient uniformity.

γ. *Dilution of the standard fluids to a convenient strength.*

With the aid of the iodine solution the strength of which we now know exactly, and the solution of hyposulphite of soda which stands in a known relation to the same, we might make any determinations of iodine. The calculation, although in principle extremely simple, is yet somewhat hampered by reason of the long decimal which expresses the quantity of iodine in 1 c. c. of the solution. It is therefore convenient to dilute the iodine solution so that 1 c. c. may exactly contain 0·005 grm. iodine. This is done by filling a litre flask therewith, and adding the necessary quantity of water; in our case 16·94 c. c., for 5 : 5·0847 :: 1000 : 1016·94. If the litre flask will hold above the mark, this 16·94 c. c., it is simply added, otherwise it is put into the dry bottle destined to receive the iodine solution, the iodine solution added, the whole shaken together, a portion of the fluid returned to the flask, shaken, poured back into the bottle, and the whole shaken again.

The solution of hyposulphite may now be diluted in a corresponding manner. In our case we should have had to add 27·11 c. c. water to 1000 c. c. of the solution, as will be seen from the following consideration :—

20·2 c. c. of the original iodine solution correspond to 20 c. c. of the hyposulphite solution.

∴ 1000 c. c. correspond to 990·1 c. c.

Now these 1000 c. c. were made up to 1016·94 by addition of water; if therefore we make up 990·1 c. c. of the hyposulphite of soda to the same bulk by addition of water we shall have equivalent solutions. Hence, to 990·1 c. c. we must add 26·84 c. c. water, or to 1000 c. c. 27·11 water.

In such cases of dilution, I always prefer to take exactly 1 litre instead of an uneven number of c. c., as in measuring the latter errors and inaccuracies may readily occur; I have therefore, above, recommended the preparation of 1200 c. c. of the fluids, so that after their determination 1000 c. c. may be sure to remain.

c. THE ACTUAL ANALYSIS.

Weigh the iodine, best in a small flask, dissolve in the iodide of potassium solution, using about 5 c. c. to 0·1 grm. of iodine, add hyposulphite solution from the burette till decoloration is just produced, then 3 or 4 c. c. starch solution, then iodine solution from a second burette to incipient blueness. The substance contains the same amount of iodine as the c. c. of iodine solution corresponding to the hyposulphite used *minus* the c. c. of the former used to destroy the excess of the latter. Where the solutions are of equal value and 1 c. c. corresponds to 0·005 grm. iodine, the calculation is in the highest degree simple; for suppose we had used 21 c. c. NaO, S_2O_2 and 1 c. c. iodine, the quantity of iodine present is 0·100 grm.

$$21-1=20, \text{ and } 20\times0{\cdot}005=0{\cdot}100.$$

d. KEEPING OF THE SOLUTIONS.

The iodine solution and the hyposulphite solution are kept in glass-stoppered bottles in a cool, dark place. The former then suffers no alteration, and the latter also is stable or only slightly liable to change. Caution demands, that the relation between the two solutions should be tested before each new series of experiments. The known amount of iodine in the iodine solution is and always remains the basis of the process.

If a fluid contains free iodine in presence of iodine in a state of combination, the former is determined in one portion, by the preceding method, and the total amount of iodine present in another portion. To this end, sulphurous acid is added until the fluid appears colorless, and then solution of nitrate of silver (§ 145, I., *a*); the mixture is digested with nitric acid. to remove any sulphate of silver that might have been thrown down along with the iodide, filtered, &c.; or the fluid is distilled with sesquichloride of iron, as directed in § 145, I., *d.*

§ 147.

4. HYDROCYANIC ACID.

I. *Determination.*

a. If you have free hydrocyanic acid in solution, mix the solution, in a rather dilute state, with a solution of nitrate of silver in excess, add a little nitric acid, allow to settle without warming, and determine the precipitated cyanide of silver either by collecting on a weighed filter, drying at 100° and weighing (§ 115, 3), or by collecting on an unweighed filter and converting into metallic silver. The latter operation is performed by igniting the precipitate in a porcelain crucible for ¼ hour, or till it ceases to lose weight (H. ROSE).

If you wish to determine in this way the hydrocyanic acid in bitter almond water or cherry laurel water, add ammonia after the addition of the solution of nitrate of silver till the fluid has become clear, and at once supersaturate slightly with nitric acid. This modification of the process is indispensable to precipitate from these fluids the whole of the hydrocyanic acid as cyanide of silver. In measuring a fluid containing hydrocyanic acid with a pipette, have a little tube filled with granulated soda-lime between the latter and the mouth.

b. LIEBIG'S *Volumetric Method.**—If hydrocyanic acid is mixed with potassa to strong alkaline reaction, and a dilute solution of nitrate of silver is then added, a permanent turbidity of cyanide of silver—or, if a few drops of solution of chloride of sodium have been added (which is always advisable), of chloride of silver—forms only after the whole of the cyanogen is converted into double cyanide of silver and potassium. The first drop of solution of nitrate of silver added in excess produces the permanent precipitate. 1 eq. silver consumed in the process corresponds, therefore, exactly to 2 eq. hydrocyanic acid ($2\,K\,Cy + Ag\,O, NO_5 = Ag\,Cy, K\,Cy + K\,O, N\,O_5$). A decinormal solution of nitrate of silver, containing consequently 10·797 grm. silver in the litre, should be used; 1 c. c. of this solution corresponds to 0·0054 of hydrocyanic acid. In examining medicinal hydrocyanic acid, 5 to 10 grm. ought to be used, but of bitter almond water about 50 grm.; if exactly 5·4 or 54 grm. are used, the c. c. of the silver solution, divided by 10, or by 100, expresses exactly the percentage of hydrocyanic acid. Medicinal hydrocyanic acid is suitably diluted first by adding from 5 to 8 volumes of water; bitter almond water also is slightly diluted; if turbid, alcohol is added, until the turbidity disappears.

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* Annal. d. Chem. u. Pharm. 77, 102.

Liebig has examined hydrocyanic acid of various degrees of dilution, and has obtained results by this method corresponding exactly with those obtained by *a*. In this method it does not matter whether the hydrocyanic acid contains an admixture of hydrochloric acid or formic acid. A considerable excess of potassa must be avoided.

If it is intended to determine cyanide of potassium by this method, a solution of that salt must be prepared of known strength, and a measured quantity used containing about 0·1 grm. of the salt. Should it contain sulphide of potassium, a small quantity of freshly precipitated carbonate of lead must be first added, and the solution filtered before proceeding to the determination.

II. *Separation of Cyanogen from the Metals.*

a. In Cyanides of the Alkali Metals.

Mix the substance (if solid, without previous solution in water) with excess of nitrate of silver solution, then add water, finally nitric acid in slight excess, allow to settle without warming, and determine the cyanide of silver as in I., *a*. The bases are determined in the filtrate after separating the excess of silver.

b. In Cyanides, which are easily decomposed by, and soluble in, Nitric Acid.

Digest for some time with nitrate of silver, stirring frequently,* then add nitric acid in moderate excess, and digest at a gentle heat, till the foreign cyanide is fully dissolved and the cyanide of silver has become pure and quite white. Then filter. As a precautionary measure it is well to test the metal obtained by long ignition of the cyanide of silver, whether it is free from those metals which were combined with the cyanogen.

c. In Cyanide of Mercury.

Precipitate the aqueous solution with sulphuretted hydrogen; the sulphide of mercury may be filtered without difficulty if a little ammonia or hydrochloric acid be added; it is determined according to § 118, 3. If the compound is in the solid condition, the cyanogen may be determined in another portion by ignition with oxide of copper, the nitrogen and carbonic acid being collected and separated (comp. organic analysis).

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* Double cyanide of nickel and potassium yields by this process a mixture of cyanide of silver with cyanide of nickel. Other double cyanides are similarly decomposed.

H. Rose and Finkener* give the following method for determining cyanogen in solutions of cyanide of mercury. Mix the solution of the cyanide of mercury with nitrate of zinc dissolved in ammonia. To 1 part of mercury-salt add about 2 parts of the zinc-salt. Add to the clear solution sulphuretted hydrogen water gradually till it produces a perfectly white precipitate of sulphide of zinc. The precipitate, which is a mixture of the sulphides of mercury and zinc, settles well. After a quarter of an hour filter it off and wash with very dilute ammonia. The filtrate contains cyanide of zinc dissolved in ammonia, together with nitrate of ammonia. It does not smell of hydrocyanic acid, and consequently no escape of the latter takes place. Mix it with nitrate of silver and then add dilute sulphuric acid in excess. The cyanide of silver is next washed a little by decantation, then—to free it from any cyanide of zinc simultaneously precipitated—heated with a solution of nitrate of silver, finally filtered off, washed, and determined after I., *a*. The precipitated sulphides may be dissolved in aqua regia, and the mercury precipitated as subchloride according to § 118, 2, *a*. The test-analyses communicated by Rose yielded excellent results.

d. In compounds decomposable by Oxide of Mercury in the Wet Way.

Many simple cyanides, and also double cyanides—both of the character of the double cyanide of nickel and potassium, and of the ferro- or ferricyanides (not, however, cobalticyanides)—may, as is well known, be completely decomposed by boiling with excess of oxide of mercury and water, all cyanogen being obtained as cyanide of mercury, and the metals passing into oxides.

H. Rose (*loc. cit.*) has shown, that Prussian blue, ferro- and ferricyanide of potassium, more particularly, may be readily analyzed in this manner.

Boil a few minutes with water and *excess* of oxide of mercury till complete decomposition is effected, add—in order to render the sesquioxide of iron and oxide of mercury removable by the filter—nitric acid in small portions, till the alkaline reaction has nearly disappeared, filter, wash with hot water, dry the precipitate, ignite—very gradually raising the heat—under a hood (with a good draught), and weigh the sesquioxide of iron remaining. In the filtrate the cyanogen is determined according to *c*, and any potassa that may be present is estimated in the fluid filtered from the cyanide of silver.

e. Determination of Metals contained in Cyanides with decomposition and volatilization of the Cyanogen.

Of the various means for completely decomposing compounds of cyanogen, especially also the double cyanides, according to H. Rose (*loc. cit.*), three particularly are worthy of recommendation, viz., concentrated sulphuric acid, sulphate of mercury, and chloride of ammonium. The nitrates seemed decidedly less suitable on account of their too violent action.

α. Decomposition by Sulphuric Acid. All cyanogen compounds, simple or double, are completely decomposed and converted into sulphates or oxides, as the case may be, if treated in a powdered condition in a platinum dish or a capacious platinum crucible with a mixture of about 3 parts concentrated sulphuric acid and 1 part water, and heated till almost all the sulphuric acid has been expelled. The residual mass is then free from cyanogen. It is dissolved in water, if necessary, with addition of hydrochloric acid, and the oxides determined by the usual methods.

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* Zeitschr. f. anal. Chem. 1, 288.

β. DECOMPOSITION BY SULPHATE OF MERCURY. Of the combinations of oxide of mercury with sulphuric acid, those suitable to our present purpose are the neutral and the basic (Turpeth mineral). The substance is mixed with 6 parts of the latter, heated in a platinum crucible gradually, and finally maintained for a long time at a red-heat, till all the mercury has volatilized, and the weight of the crucible remains constant. If alkalies are present, a little carbonate of ammonia is added during the final ignition, from time to time, in order to convert the bisulphates into neutral salts. The residue may usually be analyzed by simple treatment with water, in the case of ferrocyanide of potassium, for instance, the sulphate of potassa dissolves, and pure (alkali-free) sesquioxide of iron remains behind. The test-analyses that have been communicated yielded excellent results.

γ. DECOMPOSITION BY CHLORIDE OF AMMONIUM. Mix the substance with twice or thrice the amount of this salt and ignite the mixture moderately in a stream of hydrogen (apparatus, p. 181, fig. 47). From the cooled mass water extracts alkaline metallic chloride, while the reducible metals remain behind in the metallic state. The method is peculiarly adapted for the analysis of double cyanide of nickel and potassium and cobalticyanide of potassium, not so for iron compounds, since the iron obtained is not pure, but contains carbon.

If one of the methods described in *e* is employed, the nitrogen and carbon (the cyanogen) must be determined by combustion, if an estimation by the loss is not sufficient.

f. Determination of the Alkalies, especially of Ammonia in Soluble Ferrocyanides.

Mix the boiling solution with a solution of chloride of copper in moderate excess, filter off the precipitated ferrocyanide of copper, free the filtrate from copper by means of sulphuretted hydrogen, and then determine the alkalies (REINDEL*).

g. Volumetric Determination of Ferro- and Ferricyanogen.

α. After E. DE HAEN. This method, devised in my laboratory, is founded upon the simple fact that a solution of ferrocyanide of potassium acidified with sulphuric acid or with hydrochloric acid (and which may accordingly be assumed to contain free hydroferrocyanic acid), is by addition of permanganate of potassa converted into the corresponding ferricyanide. If this conversion is effected in a very dilute fluid, containing about 0·2 grm. ferrocyanide of potassium in from 200 to 300 c. c., the termination of the reaction is clearly and unmistakably indicated by the change of the originally pure yellow color of the fluid to reddish-yellow.

The process requires two test fluids of known strength, viz.,

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* Journ. f. prakt. Chem. 65, 452.

1. A solution of pure ferrocyanide of potassium.
2. A solution of permanganate of potassa.

The *former* is prepared by dissolving 20 grm. perfectly pure and dry crystallized ferrocyanide of potassium in water to 1 litre; each c. c. therefore contains 20 mgrm. The *latter* is diluted so that somewhat less than a buretteful is required for 10 c. c. of the solution of ferrocyanide of potassium.

To determine the strength of the permanganate of potassa solution in its action upon ferrocyanide of potassium, measure off, by means of a small pipette, 10 c. c. of the solution of ferrocyanide of potassium (containing 0·200 grm.) dilute with about 250 c. c. water, acidify with hydrochloric acid, place the glass on a sheet of white paper, and allow the permanganate to drop into the fluid, stirring it at the same time, until the change from yellow to *reddish*-yellow indicates that the conversion is complete.* Repetitions of the experiment always give very accurately corresponding results. If at any time you have reason to suspect that the permanganate has suffered alteration, recourse must be had again to this experiment.

To determine the amount of real ferrocyanide of potassium contained in any given sample of the commercial article, dissolve 5 grm. to 250 c. c.; take 10 c. c. of this solution, and examine as just directed. Suppose, in determining the strength of the permanganate, you have used 20 c. c., and you find now that 19 c. c. is sufficient, the simple rule-of-three sum,

$$20 : 0{\cdot}200 :: 19 : x$$

will inform you how much pure ferrocyanide of potassium 0·200 grm. of the analyzed salt contains. And even this small calculation may be dispensed with, by diluting the permanganate so that exactly 50 c. c. correspond to 0·200 of ferrocyanide of potassium, as, in that case, the number of half-c. c. consumed expresses directly the percentage of the ferrocyanide of potassium present in the analyzed salt.

Instead of determining the strength of the permanganate by means of pure ferrocyanide of potassium, which is unquestionably the best way, one of the methods given in § 112, 2, may also be employed; bearing in mind, in that case, that 2 eq. ferrocyanide of potassium = 422·44 (together with the water of crystallization), 2 eq. iron dissolved to protoxide = 56, and 1 eq. oxalic acid = 63 (together with the water of hydration and crystallization) are equivalent in their action upon solution of permanganate of potassa.

The analysis of soluble ferricyanides by this method is effected by reducing them to ferrocyanides, acidifying, and then proceeding in the same way as just now described. The reduction is effected as follows:—Mix the weighed ferricyanide with solution of soda or potassa in excess, boil, and add concentrated solution of sulphate of protoxide of iron gradually, and in small portions, until the color of the precipitate appears black, which is a sign that protosesquioxide of iron has precipitated. Dilute now to 300 c. c., mix, filter, and proceed to determine the ferrocyanide in portions of 50 or 100 c. c. of the fluid. As the space occupied by the precipitate is not taken into account in this process, the results are not absolutely accurate. The difference is so very trifling, however, that it may safely be disregarded.

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* If you wish at first for some additional evidence besides the change of color, add to a drop of the mixture on a plate, a drop of solution of sesquichloride of iron; if this fails to produce a blue tint, the conversion is accomplished.

Insoluble ferro- or ferricyanides, decomposable by boiling solution of potassa (as are most of these compounds), are analyzed by boiling a weighed sample sufficiently long with an excess of solution of potassa (adding, in the case of ferricyanides, sulphate of protoxide of iron), and then proceeding in the same way as directed above.

β. After E. BOHLIG.*

In the case of a fluid containing ferrocyanide of potassium, and also sulphocyanide (for instance, the red liquor of the prussiate works), the method given in *a* cannot be employed, as the hydrosulphocyanic acid also reduces permanganic acid. The following method—depending on the precipitation of the ferrocyanogen with solution of sulphate of copper—may then be used; it is accurate enough for technical purposes. Dissolve 10 grm. pure sulphate of copper to 1 litre, also 4 grm. pure dry ferrocyanide of potassium to 1 litre. Add to 50 c. c. of the latter solution (which contain 0·2 grm. ferrocyanide of potassium) copper solution from a burette to complete precipitation of the ferrocyanogen. In order to hit this point exactly, from time to time dip a strip of filter-paper into the brownish-red fluid, which will imbibe the clear filtrate, leaving the precipitate of ferrocyanide of copper behind. At first the moist strips of paper, when touched with sesquichloride of iron, become dark blue, the reaction gradually gets weaker and weaker, and finally vanishes altogether. We now know the value of the copper solution with reference to its action on ferrocyanide of potassium, and can, therefore, by its means test solutions containing unknown amounts of ferrocyanogen. If alkaline metallic sulphides are present, they are first removed by boiling with carbonate of lead. After filtering off the sulphide of lead, acidify with dilute sulphuric acid, and then proceed.

§ 148.

5. HYDROSULPHURIC ACID.

I. *Determination.*

Sulphuretted hydrogen in the free state is most readily and very accurately determined by volumetric analysis, by means of iodine; it may also be determined by conversion into a suitable sulphide or into sulphate of baryta, and weighing.

a. The method of determining free sulphuretted hydrogen by volumetric analysis, by means of a solution of iodine, was employed first by DUPASQUIER. That chemist used alcoholic solution of iodine for the purpose. But as the action of the iodine upon the alcohol gradually alters the composition of this solution, it is better to use a solution of iodine in iodide of potassium. The decomposition is as follows:

$$HS + I = HI + S$$

1 eq. I = 127 corresponds, therefore, to 1 eq. HS = 17. However, this exact decomposition can be relied upon with certainty only if the amount of sulphuretted hydrogen in the fluid to be analyzed does not exceed 0·04 per cent. (BUNSEN). Fluids containing a larger proportion of sulphuretted

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* Polytechn. Notizblatt, 16, 81.

hydrogen must therefore first be diluted to the required degree with boiled water cooled out of the contact of air.

The iodine solution of § 146 may be used for the estimation of larger quantities of sulphuretted hydrogen; for weak solutions, *e. g.*, sulphuretted mineral water, it is advisable to dilute the iodine solution of § 146 to 5 times the volume, which accordingly will give a fluid containing about 0·001 grm. iodine in the c. c.

The process is conducted as follows:—

Measure or weigh a certain quantity of the sulphuretted water, dilute, if required, in the manner directed, add some thin starch-paste, and then solution of iodine, with constant shaking or stirring, until the permanent blue color begins to appear. The result of this experiment indicates approximately, but not with positive accuracy, the relation between the examined water and the iodine solution. Suppose you have consumed, to 220 c. c. of the sulphuretted water, 12 c. c. of a solution of iodine containing 0·000918 grm. iodine in the c. c.[*] Introduce now into a flask nearly the quantity of iodine solution required, add the sulphuretted water in quantity either already determined, or to be determined, by weight or measure;[†] then to the colorless fluid add thin starch-paste, and after this iodine solution until the blue color just begins to show. By this course of proceeding, you avoid the loss of sulphuretted hydrogen which would otherwise be caused by evaporation and oxidation. In my analysis of the Weilbach water, 256 c. c. of the water required, in my second experiment, 16·26 c. c. of iodine solution, which, calculated to the quantity of sulphuretted water used in the first experiment, viz., 220 c. c., makes 13·9 c. c., or 1·9 c. c. more.

But even now the experiment cannot yet be considered quite conclusive, when made with a solution of iodine so dilute; it being still necessary to ascertain how much iodine solution is required to impart the same blue tint to the same quantity of ordinary water mixed with starch-paste, of the same temperature,[‡] and as nearly as possible in the same condition[§] as the analyzed sulphuretted water, and to deduct this from the quantity of iodine solution used in the second experiment. Thus, in the case mentioned, I had to deduct 0·5 c. c. from the 16·26 c. c. used. If the instructions here given are strictly followed, this method gives very accurate results (see Expt. No. 91).

b. Mix the sulphuretted fluid with an excess of solution of arsenite of soda, add hydrochloric acid, allow to deposit, and determine the sulphide of arsenic as directed § 127. If the quantity of sulphuretted hydrogen in the analyzed fluid is moderately large, the results obtained by this method are accurate (compare Expt. No. 91); but in the case of very dilute solutions the results are too low, as a little tersulphide of arsenic remains in solution. Hence, in my analysis of the Weilbach water, this method gave only 0·006621 and 0·006604 per 1000, whilst water taken from the well at the same time, and determined with iodine, gave 0·007025 of $H S$ per 1000. Instead of arsenious acid, solution of chloride of copper or a solution of silver may be employed as precipitant, and the sulphur determined in the sulphide of copper as sulphate of baryta (see II.), or in the sulphide of silver as chloride of silver. The results obtained by precipitating with chloride of copper are also too low, in the case of very dilute fluids.

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[*] The numbers here stated are those which I obtained in the analysis of the Weilbach water.

[†] Compare Experiment No. 91.

[‡] Annal. d. Chem. u. Pharm., 102, 186.

[§] I would recommend, in cases where the sulphuretted water contains bicarbonate of soda, to add to the ordinary water an equal quantity of this salt, as its presence has a slight influence on the appearance of the final reaction.

For the analysis of mineral waters, the method *a* will always answer best, unless presence of hyposulphites should impair its accuracy.

c. If the sulphuretted hydrogen is evolved in the gaseous state, and large quantities are to be determined, the best way is to conduct it first through several bulbed U-tubes (fig. 59, p. 308), containing an alkaline solution of arsenite of soda, then through a tube connected with the exit of the last U-tube, which contains pieces of glass moistened with solution of soda; to mix the fluids afterwards, and proceed as in *b* or *c*. If, on the other hand, we have to determine small quantities of sulphuretted hydrogen contained in a large amount of air, &c., it is well to pass the gaseous mixture in question in separate small bubbles through a very dilute solution of iodine in iodide of potassium, of known volume and strength, which is contained in a long glass tube fixed in an inclined position and protected against sunlight. The free iodine remaining is finally estimated by means of a solution of hyposulphite of soda (§ 146); the difference gives us the quantity of iodine which has been converted by sulphuretted hydrogen into hydriodic acid, and consequently corresponds to the amount of the sulphuretted hydrogen present. The volume of the gaseous mixture may be known by measuring the water which has escaped from the aspirator used. The arrangement of the absorption tube is the same as is figured in connection with the determination of carbonic acid in the air (§ 241, at the end). The thin glass tube conducting the gas into the absorption tube, however, must not be provided with an india-rubber elongation.

II. *Separation and Determination of Sulphur in Sulphides.*

A. METHODS BASED ON THE CONVERSION OF THE SULPHUR INTO SULPHURIC ACID.

1. *Methods in the Dry Way.*

a. *Oxidation by Alkaline Nitrates* (applicable to all compounds of sulphur). If the sulphides do not lose any sulphur on heating, mix the pulverized and weighed substance with 3 parts of anhydrous carbonate of soda and 4 of nitrate of potassa, with the aid of a rounded glass rod, wipe the particles of the mixture which adhere to the rod carefully off against some carbonate of soda, and add this to the mixture. Heat in a platinum or porcelain crucible (which, however, is somewhat affected by the process), at a gradually increased temperature to fusion; keep the mass in that state for some time, then allow it to cool, heat the residue with water, filter, and determine in the filtrate, which contains the whole of the sulphur as alkaline sulphate, the sulphuric acid as directed in § 132. The metal, metallic oxide, or carbonate, which remains undissolved, is determined, according to circumstances, either by direct weighing or in some other suitable way. In the presence of lead, before filtering, pass carbonic acid through the solution of the fused mass, to precipitate the small quantity of that metal which has passed into the alkaline solution.

Should the sulphides, on the contrary, lose sulphur on heating, the finely powdered compound is mixed with 4 parts carbonate of soda, 8 parts nitre, and 24 parts pure and perfectly dry chloride of sodium, and the process otherwise conducted as already given.

b. Oxidation by Chlorine Gas (after Berzelius and H. Rose, especially suitable for sulphosalts of complicated composition).

The following apparatus, or one of similar construction, is used :—

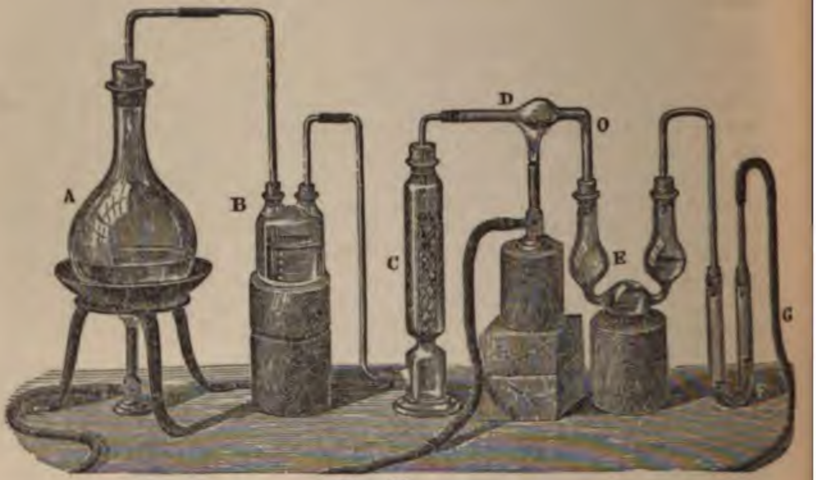

Fig. 60.

A is the evolution flask,* *B* contains concentrated sulphuric acid, *C* chloride of calcium, *D* the substance, *E* is the receiver containing water (or—in the presence of antimony—a solution of tartaric acid in dilute hydrochloric acid), *F* is a U-tube also containing water, *G* conducts the escaping chlorine into a carboy filled with moist hydrate of lime.

When the apparatus is arranged, the sulphide to be examined is weighed in a narrow glass tube sealed at one end, and subsequently cautiously transferred from this tube to the bulb, in the manner illustrated by fig. 61, so as to prevent any portion of the substance getting into the ends of the bulb-tube.

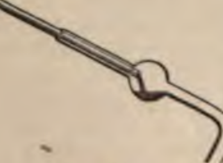

Fig. 61.

[In most cases it is more convenient to put the weighed substance into a porcelain tray (fig. 24), which is slipped into a plain piece of Bohemian combustion-tube bent like *D O*. At the close of the process the tray may be withdrawn and its contents weighed or otherwise treated.]

When the apparatus is filled with chlorine, *D* is connected with *C*, and the chlorine is allowed to act on the sulphide, at first without the aid of heat. When no further alteration is observed—the receiver *E* being full of chlorine—a very gentle heat is applied to the bulb, care being taken also to keep the tube *O* warm, securing it thus from being stopped up by the sublimate of a volatile chloride. The sulphide is completely decomposed by the chlorine, the metals being converted into chlorides, which partly remain in the bulb, partly—(viz. the volatile ones, as chloride of antimony, chloride of arsenic, chloride of mercury)—pass over into the receiver; the sulphur combines with the chlorine to chloride of sulphur, which passes over into *E*, where, coming in contact with water, it decomposes with the latter, forming hydrochloric acid and hyposulphurous acid, with separation of sulphur. The hyposulphurous acid decomposes again into sulphur and sulphurous acid, which latter is at last, by the action of the chlorine water in *E*, converted into sulphuric acid. The final result of the decomposition is consequently sulphuric acid and a greater or less amount of separated sulphur. The operation is concluded when no more products—with the exception, perhaps, of sesquichloride of iron, the complete expulsion of which need not be awaited—pass over from the bulb. Heat is then applied to the bulb-tube, proceeding from the bulb towards the bend, so as to force all the chloride of sulphur and the volatile metallic chlorides to pass over into *E*, or at least to occupy the end of the bulb-tube.

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* Pour a *perfectly cold* mixture of 45 parts of sulphuric acid and 21 of water, over one of 18 parts of chloride of sodium and 15 of *finely powdered* binoxide of manganese, and shake, when a steady evolution of chlorine will at once begin, which, when it shows signs of slackening, may be promoted by a *gentle* heat.

The apparatus is left undisturbed a short time longer, after which the tube is cut off under the bend at *O*, and the separate end, which generally contains a portion of the volatile chlorides, closed by inverting over it a glass tube sealed at one end and moistened inside. [In case a porcelain tray has been used, this is withdrawn and the entire tube is subjected to the following treatment.] The tube is now allowed to stand 24 hours, to allow the volatile chlorides to absorb moisture, which will render them soluble in water without generating heat. The metallic chlorides in the cut-off end of the tube (or tray) are then dissolved in dilute hydrochloric acid, the end (or tray) is rinsed, and the solution added to the contents of the tubes *E* and *F*; a very gentle heat is now applied until the free chlorine is expelled, and the fluid is then allowed to stand until the sulphur has solidified. The sulphur is filtered off on a weighed filter, washed, dried, and weighed. The filtrate is precipitated with chloride of barium (§ 132), by which operation the amount of that portion of the sulphur is determined which has been converted into sulphuric acid. The fluid filtered from the sulphate of baryta contains, besides the excess of chloride of barium added, also the volatile metallic chlorides; which latter are finally determined in it by the proper methods, which will be found in Section V.

The chloride remaining in the bulb-tube is either at once weighed as such (chloride of silver, chloride of lead), or where this is impracticable—as in the case of copper, for instance, which remains partly as subchloride, partly as chloride—it is dissolved in water, hydrochloric acid, nitrohydrochloric acid, or some other suitable solvent, and the metal or metals in the solution are determined by the methods already described, or which will be found in Section V. To be enabled to ascertain the weight of the bulb-tube containing the chloride of silver or chloride of lead, it is advisable to reduce the chlorides by hydrogen gas, and then dissolve the metals in nitric acid.

c. Oxidation by Oxide of Mercury (*after* BUNSEN).

This method, which will be found in detail under "the determination of sulphur in organic bodies" (§ 186, *a*, 4), is particularly suited to the estimation of sulphur in volatile compounds, or in substances which when heated lose sulphur.

2. *Methods in the Wet Way.*

*a. Oxidation of the Sulphur by Acids yielding Oxygen.**

α. Weigh the finely pulverized sulphide in a small glass tube sealed at one end, and drop the tube into a tolerably capacious strong bottle with glass stopper, which contains red fuming nitric acid (perfectly free from sulphuric acid) in more than sufficient quantity to effect the decomposition of the sulphide. Immediately after having dropped in the tube, close the bottle. When the action, which is very impetuous at first, has somewhat abated, shake the bottle a little; as soon as this operation ceases to cause renewed reaction, and the fumes in the flask have condensed, take out the stopper, rinse this with a little nitric acid, letting the rinsings run into the bottle, and then heat the latter gently.

aa. The whole of the Sulphur has been oxidized, the Fluid is perfectly clear.†

Dilute with much water, and determine the sulphuric acid formed as directed in § 132. Do not neglect to wash the precipitate thoroughly with hot water, and to ascertain, after weighing, whether it is absolutely insoluble in dilute hydrochloric acid. Separate the bases in the filtrate from the excess of the salt of baryta by the proper methods, which will be found in Section V. If any considerable amount of nitric acid has been used, evaporate the excess of the same after addition of some nitrate of potassa, before precipitating the sulphuric acid.

bb. Undissolved Sulphur floats in the fluid.

Add chlorate of potassa in small portions, or strong hydrochloric acid, and digest some time on a water bath. This process will often succeed in dissolving the whole of the sulphur. Should this not be the case, and the undissolved sulphur appear of a pure yellow color, dilute with water, collect on a weighed filter, wash carefully, dry, and weigh. After weighing, ignite the whole, or a portion of it, to ascertain whether it is perfectly pure. If a fixed residue remains (consisting commonly of quartz, gangue, &c., but possibly also of sulphate of lead, sulphate of baryta, &c.), deduct its weight from that of the impure sulphur. In the filtered fluid determine the sulphuric acid as in *aa*, calculate the sulphur in it, and add the amount to that of the undissolved sulphur. If the residue left upon the ignition of the undissolved sulphur contains an insoluble sulphate, decompose this as directed in § 132, and add the sulphur found in it to the principal amount.

In the presence of bismuth, the addition of chlorate of potassa or of hydrochloric acid is not advisable, as chlorine interferes with the determination of bismuth.

β. Mix the finely pulverized metallic sulphide, in a dry flask, by shaking, with powdered chlorate of potassa (free from sulphuric acid), and add moderately concentrated hydrochloric acid in small portions. Cover the flask with a watch-glass, or with an inverted small flask. When the whole of the chlorate of potassa is decomposed, heat gently, finally on the water-bath, until the fluid smells no longer of chlorine. Proceed now as directed in *α*, *aa*, or *bb* according to whether the sulphur is completely dissolved or not. In the latter case you must of course immediately dilute and filter. The oxidation of the sulphur may be effected also by heating with ordinary nitric acid and chlorate of potassa.

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* In presence of lead, baryta, strontia, lime, tin, and antimony, method *b* is preferable to *a*.

† This can of course be the case only in absence of metals forming insoluble salts with sulphuric acid. If such metals are present, proceed as in *bb*, as it is in that case less easy to judge whether complete oxidation of the sulphur has been attained.

γ. Strong nitrohydrochloric acid is also often used instead of the oxidizing agents named in *α* and *β*; however, with this the complete conversion of the sulphur into sulphuric acid succeeds more rarely.

b. Oxidation of the Sulphur by Chlorine in Alkaline Solution (*after* RIVOT, BEUDANT, *and* DAGUIN. Suitable also for determining the sulphur in the crude article*).

Heat the very finely pulverized sulphide or crude sulphur, for several hours with solution of potassa, free from sulphuric acid (which dissolves free sulphur, as well as the sulphides of arsenic and antimony), and then conduct chlorine into the fluid. This speedily oxidizes the sulphur; the sulphuric acid formed combines with the potassa to sulphate, which dissolves in the fluid, whilst the metals converted into oxides remain undissolved. Filter, acidify the alkaline filtrate, and precipitate the sulphuric acid from it by chloride of barium (§ 132). Arsenic and antimony pass into the alkaline solution in the form of acids, but not so lead, which is converted into binoxide, and remains completely undissolved. This method is, therefore, particularly suitable in presence of sulphide of lead. In presence of sulphide of iron, sulphate of potassa is formed at first, and hydrate of sesquioxide of iron, which, if the action of the chlorine is allowed to continue, will be converted into ferrate of potassa. As soon, therefore, as the fluid commences to acquire a red tint, the transmission of chlorine must be discontinued, and the fluid gently heated for a few moments with powdered quartz, to decompose the ferric acid.

It occasionally happens, more particularly in presence of sand, iron pyrites, oxide of copper, &c., that the process is attended with impetuous disengagement of oxygen, which almost completely prevents the oxidizing action of the chlorine. However, this accident may be guarded against by reducing the substances to be analyzed to the very finest powder.

B. METHODS BASED ON THE CONVERSION OF THE SULPHUR INTO SULPHURETTED HYDROGEN OR A METALLIC SULPHIDE.

a. The determination of the sulphur in the sulphides of the metals of the alkalies and alkaline earths soluble in water is best effected—provided they are free from excess of sulphur—by I., *b* or *c*. The bases are conveniently estimated in a separate portion, which is decomposed by evaporation with hydrochloric or sulphuric acid, or—when none but alkali-metals are present—by ignition with 5 parts of chloride of ammonium in a porcelain crucible. If the said compounds contain excess of sulphur they should be oxidized either by chlorine in alkaline solution, or treated according to *B*, *c*, or *C*; if they contain hyposulphite or sulphite, proceed according to § 168.

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* Compt. Rend. 37, 835; Journ. f. prakt. Chem. 61, 134.

b. The sulphur contained in alkaline fluids as monosulphide or hydrosulphate of the sulphide may also be determined directly by volumetric analysis, by means of a standard ammoniacal zinc or silver solution. The former is added to the solution of the sulphide of the alkali-metal until a drop coming in contact with a drop of alkaline solution of lead[*] on filter paper, no longer produces a black line (Fr. Mohr[†]). Or the latter reagent is added to the fluid—previously mixed with ammonia and warmed—till a further addition of silver solution to a filtered portion only gives a trifling turbidity (Lestelle). The methods are especially adapted to technical purposes, *e. g.*, for the estimation of the sulphide of sodium in soda-lyes, &c.

THIRD GROUP.

NITRIC ACID.—CHLORIC ACID.

§ 149.

1. Nitric Acid.

I. *Determination.*

Free nitric acid in a solution containing no other acid is determined most simply in the volumetric way, by neutralizing with a dilute solution of soda of known strength (comp. Special Part, "Acidimetry"). The following method also effects the same purpose: Mix the solution with baryta water, until the reaction is just alkaline, evaporate slowly in the air, nearly to dryness, dilute the residue with water, filter the solution which has ceased to be alkaline, wash the carbonate of baryta formed by the action of the carbonic acid of the atmosphere upon the excess of the baryta water, add the washings to the filtrate, and determine in the fluid the baryta as directed in § 101. Calculate for each 1 eq. baryta 1 eq. nitric acid. Lastly, free nitric acid may also be determined in a simple manner by supersaturating with ammonia, evaporating in a weighed platinum dish, drying the residue at 110° to 120°, and weighing the $NH_4\,O, N\,O_5$ (Schaffgotsch).

II. *Separation of nitric acid from the bases, and determination of the acid in nitrates.*

The determination of nitric acid in nitrates is an important and occasionally a difficult problem, which has of late years much occupied the attention of chemists. Before entering upon the consideration of the question, I would lay it down as a general rule, that whatever method may be selected, it should always first be tried repeatedly upon weighed quantities of a pure nitrate, that some familiarity with the details of these rather complicated processes may be acquired. Considering the great number of methods that have been proposed, I shall confine myself to describing the simplest and the best.

a Methods based on the expulsion of the Acid in the Dry Way.

α. In salts of the heavy metals or the earths, the determination of nitric acid may be effected by simple ignition of the anhydrous compound.

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[*] Made by mixing sugar of lead, Rochelle salt, and solution of soda.

[†] Lehrbuch der Titrirmethode, 2^{te} Aufl. 379.

If we are certain that the oxides remain in the same condition in which they were contained in the decomposed salt, the loss of weight indicates at once the quantity of nitric acid present.

β. In the case of nitrates, whose residue on ignition has no constant composition, or by whose ignition the crucible is much attacked (alkaline and alkaline earthy nitrates), fuse the substance (which must be anhydrous and also free from organic and other volatile bodies) with a non-volatile flux, and estimate the nitric acid from the loss. Silicic acid is the best flux, as it may be readily procured, and the execution is the most easy and the most certain to succeed. I shall describe the method in its application to nitrate of potassa or soda.

Fuse the latter at a low temperature, pour out on to a warm porcelain dish, powder and dry again before weighing. Now transfer to a platinum crucible 2 to 3 grm. powdered quartz, ignite well and weigh after cooling. Add about 0·5 grm. of the salt prepared as above, mix well, and convince yourself by the balance that nothing has been lost during mixing. The covered crucible is then exposed to a low red heat (just visible by day) for half an hour, and weighed after cooling with the cover. The loss of weight represents the quantity of nitric acid. Sulphates or chlorides are not decomposed at the given temperature; if a higher heat be applied, the latter may volatilize. The action of reducing gases must be avoided. The test-analyses, communicated by Reich,[*] as well as those performed in my own laboratory,[†] gave very satisfactory results.

b. Method based on the distillation of the Hydrate of Nitric Acid.

All nitrates may be decomposed by distillation with moderately dilute sulphuric acid. The nitric acid passing into the receiver may then be determined, according to I., volumetrically or gravimetrically. 1 to 2 grm. of the nitrate should be treated with a cooled mixture of 1 volume concentrated sulphuric acid and 2 volumes water. For 1 grm. nitre take 5 c. c. sulphuric acid and 10 c. c. water. The distillation may be performed either with a thermometer at 160° to 170° in a paraffin or sand-bath (duration of the distillation for 1 to 2 grm. nitre, 3 to 4 hours), or *in vacuo*, with the use of a water-bath. The latter process is the best. In the former, the neck of the tubulated retort (which is drawn out and bent down) is connected with a bulbed U-tube[‡] containing a measured quantity of normal soda or potassa solution (§). The distillation *in vacuo* may be conducted, without the use of an air pump, according to Finkener,[‖] as follows: transfer the measured quantity of water and concentrated sulphuric acid to the tubulated retort, and the necessary quantity of standard potassa or soda solution diluted to 30 c. c., to a flask with a narrow neck of about 200 c. c. capacity. Then, by means of an india-rubber tube, connect the flask with the retort air-tight, so that the drawn-out point of the latter may extend to the body of the flask, and—with tubulure open—heat the contents of the retort and of the flask to boiling. When the air has been expelled from the apparatus by long boiling, transfer the salt (weighed in a small tube) to the retort through the tubulure, close the latter immediately, and at the same time take away the lamp. The retort is then heated with a water-bath, the flask being kept cool.

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[*] Berg- und Hüttenmännische Zeitschrift, 1861, No. 21; Zeitschrift f. analyt. Chem. 1, 86.

[†] Zeitschrift f. analyt. Chem. 1, 181.

[‡] The bulbed U-tube will be found figured § 185.

[‖] Zeitschrift f. analyt. Chem. 1, 309.

The quantity of nitric acid that has passed over is finally ascertained by determining the still free alkali with standard acid. If it is suspected that all the nitric acid has not been driven into the receiver by one distillation, you may—by heating the flask and cooling the retort—distil the water back into the latter, and then the distillation from the retort may be repeated. The distillate thus obtained is always free from sulphuric acid, hence the results are very exact. The base remains as sulphate in the retort. In the presence of chloride add to the contents of the retort a sufficiency of dissolved sulphate of silver, or—when much chloride is present—moist oxide of silver. The nitric acid is then obtained entirely free from chlorine.

c. *Methods based on the decomposition of Nitrates by Alkalies, &c.*

α. Nitrates, whose bases are completely separated by caustic or carbonated alkalies—provided basic salts are not precipitated at the same time—may be analyzed by simple boiling with an excess of standard potassa or soda or their carbonates. After cooling, dilute to $\frac{1}{4}$ or $\frac{1}{2}$ litre, mix, allow to settle, draw off a portion of the supernatant clear fluid, determine the free alkali remaining in it, and calculate therefrom the amount consumed by the nitric acid. HAYES obtained with the nitrates of silver and bismuth good results; but with subnitrate of mercury (using carbonate of soda) the results were not so satisfactory.*

β. In nitrates, whose bases are precipitated by hydrate of baryta or lime, or by their carbonates (or by sulphide of barium), the nitric acid may be estimated with great accuracy by filtering, after precipitation has been effected, warm or cold, passing carbonic acid through the filtrate, if necessary, till all the baryta is precipitated, warming, filtering, and determining the baryta in the filtrate by sulphuric acid. 1 eq. of the same corresponds to 1 eq. of nitric acid. [In case of bismuth-salts, boil until the separated oxide is perfectly yellow. PAIGE].

γ. In many nitrates whose bases are precipitable by sulphuretted hydrogen the nitric acid may be determined according to GIBBS by adding to the salt in solution about its own weight of some neutral organic salt, *e.g.*, Rochelle salt, and throwing down the metal by HS. The filtrate and washings are brought to a definite bulk and the free acid is determined in aliquot portions alkalimetrically.†

d. *Methods based upon the decomposition of the Nitric Acid by Protochloride of Iron.*

Method of PELOUZE‡ and FRESENIUS. The decomposition is as follows:

$$6\,\mathrm{Fe\,Cl} + \mathrm{K\,O,\,N\,O_5} + 4\,\mathrm{H\,Cl} = 4\,\mathrm{H\,O} + \mathrm{K\,Cl} + 3\,\mathrm{Fe_2Cl_3} + \mathrm{N\,O_2}.$$

α. Select a tubulated retort of about 200 c. c. capacity, with a long neck, and fix it so that the latter is inclined a little upwards. Introduce into the body of the retort about 1·5 grm. fine pianoforte wire, accurately weighed, and add about 30 or 40 c. c. pure fuming hydrochloric acid. Conduct now through the tubulure, by means of a glass tube reaching only about 2 cm. into the retort, hydrogen gas washed by solution of potassa, or pure carbonic acid, and connect the neck of the retort with a U-tube containing some water. Place the body of the retort on a water-bath, and heat gently until the iron is dissolved. Let the contents of the retort cool in the current of hydrogen gas or carbonic acid; increase the latter, and drop in, through the neck of the retort, into the body, a small tube containing a weighed portion of the nitrate under examination, which should not contain more than about 0·200 grm. of nitric acid. After restoring the connection between the neck and the U-tube, heat the contents of the retort in the water-bath for about a quarter of an hour, then remove the water-bath, heat with the lamp to boiling, until the fluid, to which the nitric oxide had imparted a dark tint, shows the color of sesquichloride of iron, and continue boiling for some minutes longer. Care must be taken to give the fluid an occasional shake, to prevent the deposition of dry salt on the sides of the retort. Before you discontinue boiling, increase the current of hydrogen or carbonic acid gas, that no air may enter through the U-tube when the lamp is removed. Let the contents cool in the current of gas, dilute copiously with water, and determine the iron still present as protochloride by permanganate (see Note, p. 198)—168 of iron converted by the nitric acid from the state of proto- to that of sesquichloride correspond to 54 of nitric acid. My test-analyses of pure nitrate of potassa gave 100·1—100·03—100·03, and 100·05 instead of 100.[*] [The remaining sesquioxide may also be determined by hyposulphite of soda, p. 203, 3 *b*.].

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* H. Rose, Zeitschrift f. analyt. Chem. 1, 306.

† Am. Jour. Sci. xliv., 209.

‡ Journ. f. prakt. Chem. 40, 324.

[*β*. Schlösing's method,[†] modified by Frühling and Grouven.[‡]

The following method, employed by Schlösing, more particularly to determine nitric acid in tobacco, and which affords this very important advantage, that it may be used in presence of organic matter, has successfully passed through the ordeal of numerous and searching experiments.

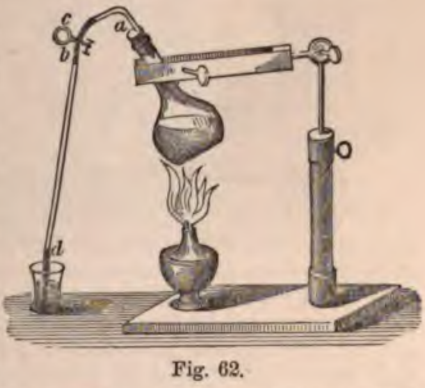

Fig. 62.

The dissolved nitrate is introduced into a flask of 400 c. c. capacity, fig. 62, which is connected, by means of an india-rubber stopper, with a narrow glass tube, *a*, which is joined by means of a rubber tube 8 cm. long, with another glass tube that is again terminated at *d*, by a piece of rubber tube. At *c* a pinch-cock is placed. The solution of the nitrate, which must be neutral or alkaline, is heated to boiling, *d* being stationed in a beaker of water, until the atmospheric air is perfectly expelled from the apparatus. When the vapors that pass over completely condense in *d*, the pinch-cock *c* is closed and the lamp is removed. Water immediately rises in the tube and fills it entirely to *c*. Shortly the vapors in the flask condense, as shown by the collapse of the rubber tube at *c*. At this moment the tube *d* is removed from the water and dipped in a glass containing a solution of protochloride of iron in hydrochloric acid.

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[*] Annal. d. Chem. u. Pharm. 106, 217.

[†] Annal. de Chim. 3 sér. tom. 40, 479; Journ. f. prakt. Chem. 62, 142.

[‡] Versuchs-Stationen, IX. 14.

The pinch-cock is cautiously opened so as to allow the protochloride to enter the flask slowly. When sufficient of the iron solution has been introduced, the pinch-cock is closed, and *d* is brought into a vessel of hydrochloric acid, and portions of this are made to enter the flask in the same manner repeatedly until the tubes are completely washed of all protochloride. In these operations, as in all the subsequent transfers, it is needful to exclude all traces of air, which is easy, provided the drop of liquid that hangs to *d* when it is carried from one liquid to another, is not allowed to fall off. Finally, the tube is rinsed once by allowing boiling water to recede, and then, the cock being closed, the tube *d*, still full of water, is passed into the lateral tubulure of the receiver, fig. 63, which stands immersed in mercury.

The flask is again gently heated and its contents immediately boil with violent thumping. The solution becomes black, and shortly the collapsed rubber tube at *c* shows that there is interior pressure. As soon as this is evident, open the cock and allow the nitric oxide gas to pass over into the receiver.

The receiver, fig. 63, has a rough-ground neck, which is connected by rubber, *f*, with a brass cock;* the latter is likewise joined by rubber to a short glass tube, *g*. Into this receiver, the cock being open, some water, freed from air by long boiling and cooled in a closed vessel, is introduced by a tall funnel-tube fitted into the tubulure, and then mercury is poured in until it fills the vessel up to the lower edge of the rubber, *f*. In this operation the cock and small tube, *g*, should be overfilled with the water previously added. The receiver is thus empty of all air, and stands with the tubulure covered with mercury, as in fig. 64.

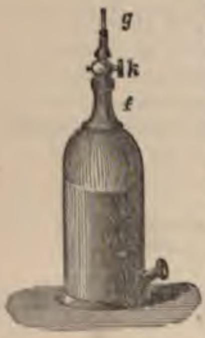

Fig. 63.

By means of a pipette, having a narrow rubber tube slipped over its tip, about 50 c. c. of thick and well-boiled milk of lime are passed into the receiver through the tubulure. This is to absorb the hydrochloric acid which boils over from the flask, and the receiver is shaken to facilitate the absorption.

The nitric oxide, expelled from the flask by continual boiling, gathers in the receiver in a state of purity. The period of its complete transfer is exactly marked by the deposition of the milk of lime, which is thrown into agitation by the passage of a permanent gas, but quietly condenses or absorbs steam and hydrochloric acid. The completion of the reaction is also indicated, in case pure nitrates are employed, by the liquid in the flask assuming the color of pure sesquichloride of iron. When dark vegetable extracts are under analysis this indication is not offered.

Should the nitric oxide come off in quantity greater than the receiver can contain at once, the cocks are closed and the lamp is removed from under the flask.

The receiver is then emptied, as is subsequently described, charged anew with water, mercury, and milk of lime, reconnected, and the boiling resumed.

When the nitric oxide has been completely collected in the receiver

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[* Such receivers (Bunsen's gasometer) may be procured with a glass stopcock.]

it must be transferred to a second flask, to be converted into nitric acid.

This flask, fig. 64, arranged like the one already described, contains at first about 100 c. c. of pure water, which is boiled to expel all atmospheric air, and while still boiling vigorously is connected with the receiver by passing the end of the tube *x* over the glass tube *g*, of the latter. The lamp is then removed, and when collapse of the rubber tube takes place, the brass stopcock of the receiver is slightly and cautiously opened and the gas allowed to recede into the flask until the milk of lime reaches the lower edge of *f*. The cock is then closed and the last portions of nitric oxide are rinsed into the flask by passing into the receiver a few (20–30) c. c. of pure hydrogen (washed by passing through oil of vitriol and milk of lime), and allowing this to recede in the same way. This rinsing is repeated three or four times. The rubber tube is now closed by a pinch-cock at *y*, and disconnected from the receiver. It is then united in the same manner with a gas-holder containing pure oxygen under pressure, and the gas is made to enter the flask. It is absorbed with the appearance of red fumes and the formation of nitric acid. After half an hour or so, the flask being occasionally shaken, the nitric acid is dissolved in the water of the flask, and may be estimated by a standard alkaline solution, § —.

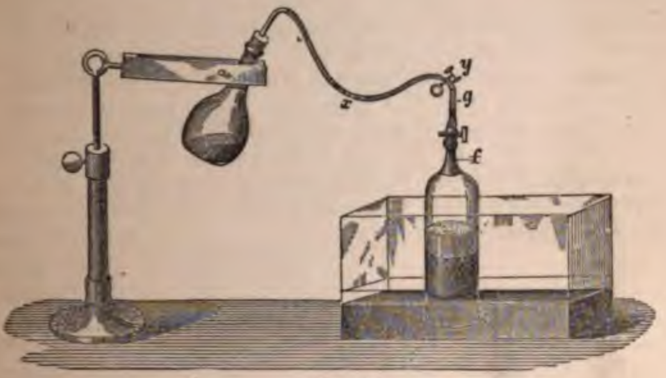

Fig. 64.

FRÜHLING and GROUVEN, who applied this method to the estimation of nitrates in plants, extracted the dried vegetable with alcohol of 50 per cent., evaporated the solution to a small volume, precipitated with caustic lime, and employed the filtrate for the analysis. For details, see their paper, *loc. cit.*]

[*e. Method based on the conversion of the Nitric Acid into Ammonia.*

If a nitrate be placed cold in an acid, or be heated in an alkaline fluid in which nascent hydrogen is evolved in sufficient quantity, all the nitric acid may be converted into ammonia, so that from the amount of the latter the quantity of the nitric acid may be accurately deduced, NESBIT* was the first to arrange a method for the determination of our acid on this principle. Afterwards Schulze,[*] Harcourt,[†] and Siewert,[‡] suggested processes with the same object. Nesbit reduces with zinc in acid solution. The others reduce in alkaline solution, Schulze with platinized zinc, Harcourt and Siewert with zinc and iron filings.

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* Quart. Journ Chem. Soc. 1, p. 281.

To reduce 0·65 grm. (10 grains, of nitre, Nesbit directs to place 15 or 20 grm. of thin clean fragments of zinc in a flask with some water. From 15 to 20 c.c. of hydrochloric acid, sp. gr. 1·17, are poured out into a small measure, and about one-tenth part is added to the zinc and water. When effervescence has fairly commenced, a portion of the nitrate, previously dissolved in water, is added to the mixture. The temperature must be kept low, if necessary, by placing the vessel in cold water. After a short period a little more acid is added, and then a little nitrate, until all the solution of the nitrate and the washings are poured in and about one-fourth of the acid is left. Care should be taken that for the first hour the effervescence be slow. When the whole of the solution of the nitrate is poured in, the remainder of the acid must be added from time to time, and the whole left until effervescence ceases. The liquid is separated from the undissolved zinc which is washed with the smallest quantity of water, and the liquid is distilled with hydrate of lime or potash, and the ammonia estimated as directed § 99, 3. Instead of distilling off the ammonia, the acid solution is brought to a volume of, say 50 c.c., and 10 c. c. are treated in the azotometer according to § 99, 4. The results are good if the directions are followed strictly. It is especially needful not to allow the reducing action to proceed too vigorously, as otherwise the mixture gets warm and binoxide of nitrogen escapes. A similar process of reduction has given good results in the hands of Krocker and Dietrich.[‖]

Siewert employs to about 1 grm. nitre, 4 grm. iron filings and 8—10 grm. zinc-filings, and also 16 grm. solid hydrate of potassa and 100 c. c. alcohol, 0·825 sp. gr. By the use of alcohol the danger of the boiling fluid receding is got rid of. His apparatus consists of a flask of 300—350 c. c. capacity with evolution tube, which leads to the flasks represented in fig. 65. The capacity of each is 150—200 c. c.; they contain normal acid. The connecting-tube *b* is ground obliquely at both ends, *c* serves during the operation to hold a strip of litmus paper, and after it to enable the analyst to transfer the fluid from one flask to the other at will. After the apparatus has been put together, the disengagement of gas may be allowed to go on in the cold, or it may be assisted from the first by a small flame. After the lapse of half-an-hour the ammonia formed begins to pass over in proportion as the alcohol distils off. As soon as the latter is fully removed from the evolution flask, heat is applied with great caution—to drive out the last traces of ammonia—till steam appears in the evolution tube, or 10—15 c. c. alcohol are rapidly introduced once or twice into the evolution flask and distilled off. The ammonia is determined as above. Test-analyses good.

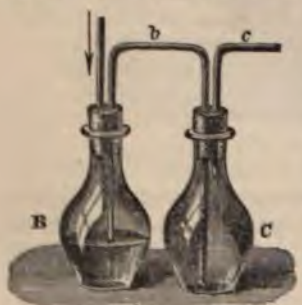

Fig. 65.

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[*] Chem. Centralblatt, 1861, 657 u. 833.
[†] Journ. of the Chem. Soc. xv. 385.
[‡] Annal. d. Chem. Pharm. 125, 293.
[‖] Fres. Zeit. iii., 69.

f. Methods in which the Nitrogen of the Nitric Acid is separated and measured in the gaseous form.

hese methods are more particularly suitable for analyzing nitrates ch are decomposed by ignition into oxide or metal and oxides of ogen; they will be found in the Section on the Ultimate Analysis of anic Bodies, § 184. MARIGNAC employed them to analyze compounds itric acid with suboxide of mercury. BROMEIS analyzed nitrite, &c., ead by a similar method, recommended by BUNSEN. In cases where intended to determine the water of the analyzed nitrate in the direct , such methods are almost indispensable.*

§ 150.

2. CHLORIC ACID.

I. *Determination.*

ree chloric acid in aqueous solution may be determined by converting nto hydrochloric acid by the agency of nascent hydrogen (II., *c*), determining the acid formed, as directed in § 141; or by saturating solution of soda, evaporating the fluid, and treating the residue as cted in II., *a* or *b*.

II. *Separation of Chloric Acid from the Bases and Determination of the Acid in Chlorates.*

. After BUNSEN.† When warm hydrochloric acid acts upon chlos, the latter are reduced; as this reduction is not attended with ration of oxygen, the following decompositions may take place :—

$$\begin{cases}\mathrm{Cl\,O}\\ \mathrm{Cl\,O_3}\\ \mathrm{H\,O}\end{cases} \quad \left.\begin{matrix}\mathrm{ClO_5}\\ \mathrm{2\,HCl}\end{matrix}\right\}\begin{matrix}\mathrm{3\,ClO}\\ \mathrm{2\,HO}\end{matrix} \quad \left.\begin{matrix}\mathrm{ClO_5}\\ \mathrm{3\,HCl}\end{matrix}\right\}\begin{matrix}\mathrm{2\,ClO}\\ \mathrm{2\,Cl}\\ \mathrm{3\,HO}\end{matrix} \quad \left.\begin{matrix}\mathrm{ClO_5}\\ \mathrm{4\,HCl}\end{matrix}\right\}\begin{matrix}\mathrm{ClO}\\ \mathrm{4\,Cl}\\ \mathrm{4\,HO}\end{matrix} \quad \left.\begin{matrix}\mathrm{ClO_5}\\ \mathrm{5\,HCl}\end{matrix}\right\}\begin{matrix}\mathrm{6\,Cl}\\ \mathrm{5\,HO}\end{matrix}$$

ich of these products of decomposition may actually be formed, ther all or only certain of them, cannot be foreseen. But no matter ch of them may be formed, they all of them agree in this, that, in tact with solution of iodide of potassium, they liberate for every 1 chloric acid in the chlorate, 6 eq. iodine. 762 of iodine liberated espond accordingly to 75·46 of chloric acid. The analytical process onducted as described § 142, 1.

. After SESTINI.‡ To the concentrated aqueous solution of the ghed chlorate add a piece of zinc and then some pure dilute sulphuric and allow to stand for some time (with 0·1 grm. chlorate of potassa, an hour is sufficient). By the nascent hydrogen the chloric acid is verted into hydrochloric acid, which, after removal and rinsing of the , is determined according to § 141. To use the volumetric method 41, *b*, *a*), the sulphuric acid is first precipitated with nitrate of baryta, the zinc and excess of baryta with carbonate of soda, the liquid is red and neutralized, then chromate of potassa is added, and finally dard silver solution.

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* See also Gibbs, Am. Journ. Sci., xxxvii. 350.

† Annal. d. Chem. u. Pharm. 86, 282.

‡ Zeitschrift f. analyt. Chem. 1, 500.

ses are determined with advantage in a separate portion, g the chlorate either by very cautious ignition, or by warm-drochloric acid into chloride.

ation of *hypochlorous acid* will be described in the Special "Chlorimetry."

SECTION V.

SEPARATION OF BODIES.

§ 151.

In the previous Section we have considered the methods employed for the determination of bases and acids, when only one base or one acid is present. In the present Section we shall treat of the separation of bodies, *i. e.*, the determination of the bases and acids, when several bases or acids are present.

The separation of bodies may be effected in three ways, viz., *a*, by *direct analysis*; *b*, by *indirect analysis*; *c*, by *estimation by difference.*

By *direct analysis*, we understand the actual separation of the bases or acids. Thus, we separate potash from soda by bichloride of platinum; copper from tin by nitric acid; arsenic from iron by sulphuretted hydrogen; iodine from chlorine by nitrate of protoxide of palladium; phosphoric acid from sulphuric acid by baryta; carbon from nitrate of potassa by water, &c., &c. In direct analysis we render the body to be estimated insoluble, while the other remains in solution, or *vice versâ*, or we volatilize it, leaving the others behind, or we effect actual separation in some other manner. This is the mode of analysis most frequently employed. It generally deserves the preference where choice is permitted.

We term an analysis *indirect*, if it does not effect the actual separation of the bodies we wish to determine, but causes certain changes which enable us to calculate the quantities of the bases or acids present. Thus the quantity of potash and soda in a mixture of the two may be determined by converting them into sulphates, weighing the latter, and estimating the sulphuric acid (§ 152, 3).

Finally, if we weigh two bodies together, determine one of them, and subtract its weight from that of the two, we shall find the weight of the other body. In this case the second body is said to be *estimated by difference.* Thus, alumina may be determined when mixed with sesquioxide of iron, by weighing the mixture and estimating the iron volumetrically.

Indirect analysis and estimation by difference may be employed in an exceedingly large number of cases; but their use is as a rule only to be recommended, where good methods of true separation are wanting. The special cases in which they are preferable to direct analysis cannot be all foreseen; those alone are pointed out which are of more frequent occurrence. As regards the calculations required in indirect analysis I have given general directions under the "Calculation of Analysis;" wherever it appeared judicious, I have added the necessary directions to the description of the method itself.

I have retained our former subdivision into groups, and, as far as practicable, systematically arranged, first, the general separation of all the bodies belonging to one group from those of the preceding groups; secondly, the separation of the individual bodies of one group from all or from certain bodies of the preceding groups; and finally, the separation of bodies belonging to one and the same group from each other. I think I need scarcely observe that the general methods which serve to separate the whole of the bodies of one group from those of another group, are also applicable to the separation of every individual body of the one group from one or several bodies of the other group. It must not be understood that the more special methods are necessarily in all cases preferable to the more general ones. As a rule it must be left to individual chemists to decide for themselves in each special case which method should be adopted. With respect to the general methods for separating one group from another, I would observe that those adduced appeared to me more adapted to the purpose than others, but still there may be other that are equally suitable, and in special cases even more so. A wide field is here open to the ingenuity of the analyst.

The methods given for the separation of both bases and acids are generally based upon the supposition that they are in the free state, and in the form of salts soluble in water. Wherever this is not the case, special mention is made of the circumstance.

From among the host of proposed methods, I have, as far as practicable, chosen those which have been sanctioned by experience and are distinguished for accurate results. In cases where two methods were on a par with each other as regards these two points, I have either given both, or selected the more simple one. Methods which experience has shown to be defective or fallacious have been altogether omitted. I have endeavored to point out, as far as possible, the particular circumstances under which either the one or the other of several methods deserve the preference.

Where the accuracy of an analytical method has been established already, in Section IV., no further statements are made on the subject here. Paragraphs of former Sections deserving particular attention are referred to in parentheses.

The extension of chemical science introduces almost every day new analytical methods of every description, which are, rightly or wrongly, preferred to the older methods; the present time may therefore be looked upon in this, as in so many other respects, as a period of transition, in which the new strives more than ever to overcome and supplant the old. I make this remark to show the impossibility of always adding to the description of a method an opinion of its usefulness and accuracy, and also to point out the importance, under such circumstances, of a proper systematic arrangement. I have in this Section generally arranged the various analytical methods upon the basis of their scientific principles, firmly persuaded that this will greatly tend to facilitate the study of the science, and will lead to endeavors to apply known principles to the separation of other bodies besides those to which they are already applied, or to apply new principles where experience has proved the old ones fallacious, and the methods based on them defective.

I conclude these introductory remarks, with the important caution to the student, *never to look upon a separation as successfully accomplished, before he has convinced himself that the weighed precipitates, &c., are pure, and free from those bodies from which it was intended to separate them.*

I. SEPARATION OF THE BASES FROM EACH OTHER.

FIRST GROUP.

POTASSA—SODA—AMMONIA—(LITHIA).*

§ 152.

Index :—The Nos. refer to those in the margin.
Potassa from soda, 1, 5.
" " ammonia, 3, 4.
Soda from potassa, 1, 5.
" " ammonia, 3, 4.
Ammonia from potassa, 3, 4.
" " soda, 3, 4.
(*Lithia* from the other alkalies, 6, 7, 8.)

1. *Methods based upon the different Degrees of Solubility in Alcohol, of the Double Chlorides of the Alkali Metals and Bichloride of Platinum.*)

a. POTASSA FROM SODA.

1 It is an indispensable condition in this method that the two alkalies should exist in the form of chlorides. If, therefore, they are present in any other form, they must be first converted into chlorides, which in most cases may be effected by evaporation with hydrochloric acid in excess; in the case of nitrates the evaporation with hydrochloric acid must be repeated 4—6 times till the weight of the gently ignited mass ceases to diminish. In presence of sulphuric acid, phosphoric acid, and boracic acid, this simple method will not answer. For the methods of separating the alkalies from the two latter acids, and converting them into chlorides, see §§ 135 and 136. The presence of sulphuric acid being a circumstance of rather frequent occurrence, the way of meeting this contingency is given below (**2**).

Determine the total quantity of the chloride of sodium and chloride of potassium † (§§ 97, 98), dissolve in a small portion of water, add an excess of a concentrated neutral solution of bichloride of platinum in water, evaporate on the water-bath nearly to dryness (the double chloride of platinum and sodium should not lose its water of crystallization), treat the residue with alcohol of from ·86 to ·87 sp. gr., cover the beaker or dish with a glass plate, and allow to stand a few hours, with occasional stirring. If the supernatant fluid appears of a deep yellow color, this is a proof that a sufficient quantity of bichloride of platinum has been used to precipitate the whole of the potassium. When the precipitate has settled, pour off the clear fluid through a weighed filter and examine the precipitate most minutely, if necessary, with the aid of a microscope. If it is a heavy yellow powder (sufficiently magnified, small octahedral crystals, it is the pure chloride of platinum and potassium.* Then transfer it—best with the aid of the filtrate—to the filter, wash it with spirit of ·86 to ·87 sp. gr. and proceed according to § 97. If, on the contrary, white saline particles (chloride of sodium) are to be seen mixed with the yellow crystalline powder, bichloride of platinum has been wanting, the whole of the chloride of sodium not having been completely converted into chloride of sodium and platinum. In this case the precipitate in the dish must be treated with some water, till all the chloride of sodium is dissolved, a fresh portion of bichloride of platinum is added, the whole evaporated nearly to dryness, and the above examination repeated. The quantity of the soda is usually estimated by subtracting from the united weight of the chloride of sodium and chloride of potassium the weight of the latter, calculated from that of the potassio-bichloride of platinum.

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* With regard to the separation of the oxides of cæsium and rubidium from the other alkalies, see Watts' Dictionary of Chemistry, 1. p. 1113.

† Never weigh the chlorides of the alkali metals before you have convinced yourself of their purity by dissolving them in water, which should give a clear solution, and testing this solution with ammonia and carbonate of ammonia, which must throw down no precipitate. It may be thought, perhaps, that a matter so simple need not be mentioned here; still, I have found that neglect in this respect is by no means uncommon.

To make quite sure that the potassa has completely separated, it is advisable to add to the filtrate some water, some more bichloride of platinum, and, if the quantity of soda is only small, also some chloride of sodium; evaporate on the water-bath nearly to dryness, at a temperature not exceeding 75° (BISCHOF), and treat the residue in the manner just described. In order to diminish the solvent action of the spirit on the chloride of potassium and platinum, $\frac{1}{5}$ ether may be now mixed with it. Should this operation again leave a small undissolved residue of chloride of potassium and platinum, it is filtered off, best on a separate filter, determined by itself, and the number added to the principal amount.

I prefer subjecting the filtrate to this examination, to the process of evaporating it to dryness, igniting the residue with addition of some oxalic acid, or in a current of hydrogen, extracting with water and determining the chloride of sodium in the solution obtained; since, after all, the estimation of the soda here is only *apparently* direct: if the chloride of potassium has not completely separated, the portion still remaining in the filtrate will, of course, be obtained now mixed with the chloride of sodium. The latter method can therefore only afford a control to determine whether a loss of substance has been sustained in the operation. Instead of the process given for the direct determination of soda, the filtrate containing the double chloride of platinum and sodium may also be evaporated to dryness with addition of sulphuric acid, the residue ignited, the sulphate of soda extracted with water and determined according to § 98, 1 (A. MITSCHERLICH).

Should the solution contain sulphuric acid, it may be in presence of hydrochloric acid or of some volatile acid, convert the alkalies first into neutral sulphates (§§ 97, 98), and weigh them as such. Dissolve in a little water, and add an alcoholic solution of chloride of strontium, *slightly* in excess. (The quantity of spirit of wine in the fluid must not be so large as to precipitate chloride of sodium or chloride of potassium.) Allow to deposit, filter, and wash the sulphhate of strontia (which if weighed yields an exact control of the analysis—compare § 152, 3) with weak spirit of wine, until the washings no longer leave 2 a residue upon evaporation on a watch-glass; evaporate the filtrate until the spirit of wine is completely driven off, dissolve the residue in a very small quantity of water, add bichloride of platinum, and proceed as directed above. The minute portion of chloride of strontium added in excess dissolves, either in that form, or as strontio-bichloride of platinum, together with the sodio-bichloride of platinum, in spirit of wine.

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* If small tesseral crystals are visible of a dark orange yellow color, and relatively large size, and appearing transparent by transmitted light, then the double chloride contains chloride of platinum and lithium (Jenzsch).

Instead of this method, the following process may be resorted to:—Dissolve the sulphates of the alkalies in water, and add baryta water, free from alkali, as long as a precipitate forms; allow to deposit, filter, wash the precipitate, and conduct carbonic acid into the filtrate, to throw down the excess of baryta; heat to boiling, filter the precipitated carbonate of baryta, wash, add hydrochloric acid to the filtrate, and evaporate to dryness.

Repeated experiments have shown that the process of separating potassa and soda, as described above, gives always a little less potassa than is really present. If the process is properly conducted, the loss of potassa amounts to no more than 1 per cent. I have found that it is usually greater in cases where the concentrated solution of the metallic chlorides is mixed with bichloride of platinum, and then with a rather large quantity of alcohol. [See also FINKENER, Pogg. Ann. xxix., p. 637.]

2. *Methods based upon the Volatility of Ammonia and its Salts.*

AMMONIA FROM SODA AND POTASSA.

a. The salts of the alkalies to be separated contain the same volatile acid, and admit of the total expulsion of their water by drying at 100°, *without losing ammonia* (*e. g.*, the metallic chlorides). **3**

Weigh the total mass of the salts in a platinum crucible, and heat with the lid on, gently at first, but ultimately for some time to faint redness; let the mass cool, and weigh. The decrease of weight gives the quantity of the ammonia salt. If the acid present is sulphuric acid, you must, in the first place, take care to heat very gradually, as otherwise you will suffer loss from the decrepitation of the sulphate of ammonia; and, in the second place, bear in mind that part of the sulphuric acid of the sulphate of ammonia remains with the sulphates of the fixed alkalies, and that you must accordingly convert them into neutral salts, by ignition in an atmosphere of carbonate of ammonia, before proceeding to determine their weight (compare §§ 97 and 98). Chloride of ammonium cannot be separated in this manner from sulphates of the fixed alkalies, as it converts them, upon ignition, partly or totally into chlorides.

b. Some one or other of the conditions given in a is not fulfilled.

4 If it is impracticable to alter the circumstances by simple means so as to make the method *a* applicable, the fixed alkalies and the ammonia must be estimated separately in different portions of the substance. The portion in which it is intended to determine the soda and potassa is gently ignited until the ammonia is completely expelled. The fixed alkalies are converted, according to circumstances, into chlorides or sulphates, and treated as directed in **1** or **5**. The ammonia is estimated, in another portion, according to § 99, 3

3. *Indirect Method.*

POTASSA FROM SODA.

Convert both alkalies into chlorides (§ 97, 2), and weigh; estimate the chlorine (§ 141); and calculate the quantities of the soda and potassa from these data (see "Calculation of Analyses," § 197).

The indirect method of determining potassa and soda is applicable [whenever the mixed chlorides can be obtained in a state of purity. It is very accurate and expeditious*], particularly if the chlorine is determined volumetrically (§ 141, I., *b*).

Supplement to the First Group.

SEPARATION OF LITHIA FROM THE OTHER ALKALIES.

Lithia may be separated from *potassa* and *soda* in the indirect way, or by either of the following two methods:—

a. Treat the nitrates or the chlorides, dried at 120°, with a mixture of equal volumes of absolute alcohol and anhydrous ether, digest at least for twenty-four hours, with occasional shaking (the salts must be completely disintegrated), decant on to a filter, and treat the residue again several times with smaller portions of the mixture of alcohol and ether. Determine, on the one part, the undissolved potassa and soda salts; on the other, the dissolved lithia salt, by distilling the fluid off, and converting the residue into sulphate. This method is apt to give too much lithium, as the potassa and soda salts, especially the chlorides, are not absolutely insoluble in a mixture of alcohol and ether. The results may be rendered more accurate by treating the impure lithia salt, obtained by distilling off the ether and alcohol, once more with alcohol and ether, with addition of a drop of nitric or hydrochloric acid, adding the residue left to the principal residue, and then converting the lithia salt into sulphate. If the salts, which it is intended to treat with alcohol and ether, have been ignited, however so gently, caustic lithia is formed—in the case of the chloride by the action of water—and carbonate of lithia by attraction of carbonic acid; in that case, it is necessary, therefore, to add a few drops of nitric, or, as the case may be, hydrochloric acid, in the process of digestion. The separation of the chlorides of the alkali metals by a mixture of ether and spirit was originally recommended by RAMMELSBERG.†

If we have to separate the sulphates, they must be converted into nitrates or chlorides before they can be subjected to the above method. This conversion may be effected by one of the processes given in **2**. Instead of the alcoholic solution of chloride of strontium you may use an aqueous solution of nitrate of strontia with addition of alcohol.

b. Weigh the mixed alkalies, best in form of sulphates, and then determine the lithia as phosphate according to § 100. If the quantity of lithia is relatively very small, convert the weighed sulphates into chlorides (**6**), separate, in the first place, the principal amount of the potassa and soda by means of alcohol (§ 100), and then determine the lithia (MAYER ‡).

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* COLLIER, Am. Jour. Sci. (2) xxxvii. 344.

† Pogg. Annal. 66, 79.

‡ Annal. d. Chem. u. Pharm. 98, 193.

8 The separation of lithia from *ammonia* may be effected like that of potassa and soda from ammonia (**3** and **4**).

SECOND GROUP.

BARYTA—STRONTIA—LIME—MAGNESIA.

I. Separation of the Oxides of the Second Group from those of the First.

§ 153.

Index:—The Nos. refer to those in the margin.
Baryta from potassa and soda, 9, 11.
“ “ ammonia, 10.
Strontia from potassa and soda, 9, 12.
“ “ ammonia, 10.
Lime from potassa and soda, 9, 13.
“ “ ammonia, 10.
Magnesia from potassa and soda, 14—19.
“ “ ammonia, 10.

A. *General Method.*

1. The whole of the Alkaline Earths from Potassa and Soda.

9 *Principle: Carbonate of ammonia precipitates, from a solution containing chloride of ammonium, only baryta, strontia, and lime.*

Mix the solution, which contains the bases as chlorides, with a sufficient quantity of chloride of ammonium to prevent the precipitation of the magnesia by ammonia; dilute considerably, add some ammonia, then carbonate of ammonia in slight excess, let the mixture stand covered for 2 hours in a warm place, filter, and wash the precipitate with water to which a few drops of ammonia have been added.

The *precipitate* contains the *baryta*, *strontia*, and *lime;* the *filtrate* the *magnesia* and the *alkalies*. So at least we may assume in cases where the highest degree of accuracy is not required. Strictly speaking, however, the solution still contains exceedingly minute traces of lime and somewhat more considerable traces of baryta, as the carbonates of these two earths are not absolutely insoluble in a fluid containing chloride of ammonium; the precipitate also may contain possibly a little carbonate of ammonia and magnesia. Treat the precipitate according to § 154, and the filtrate—in rigorous analyses—as follows: add 3 or 4 drops (but not much more) of dilute sulphuric acid, then oxalate of ammonia, and let the fluid stand again for 12 hours in a warm place. If a precipitate forms, collect this on a small filter, wash, and treat on the filter with some dilute hydrochloric acid, which dissolves the oxalate of lime, and leaves the sulphate of baryta undissolved. Since a little oxalate of magnesia may have separated with the former, add some ammonia to the hydrochloric solution, filter after the precipitate has settled, and mix the filtrate with the principal filtrate.

Evaporate the fluid containing the *magnesia* and the *alkalies* to dryness, and remove the ammonia salts by gentle ignition in a covered crucible, or in a small covered dish of platinum or porcelain.* In the residue, separate the magnesia from the alkalies by one of the methods given (**14**—**19**).

2. THE WHOLE OF THE ALKALINE EARTHS FROM AMMONIA.—The same principle and the same process as in the separation of potassa and soda from ammonia (**3** and **4**). **10**

B. *Special Methods.*

SINGLE ALKALINE EARTHS FROM POTASSA AND SODA.

1. BARYTA FROM POTASSA AND SODA.

11 Precipitate the baryta with dilute sulphuric acid (§ 101, 1, *a*), evaporate the filtrate to dryness, and ignite the residue, with addition towards the end of carbonate of ammonia (§ 97, 1 and § 98, 1). Take care to add a sufficient quantity of sulphuric acid to convert the alkalies also completely into sulphates.

This method is, on account of its greater accuracy, preferable to the one in **9**, in cases where the baryta has to be separated only from one of the two fixed alkalies; but if both alkalies are present, the other method is more convenient, since the alkalies are then obtained as chlorides.

2. STRONTIA FROM POTASSA AND SODA.

12 Strontia may be separated from the alkalies, like baryta, by means of sulphuric acid; but this method is not preferable to the one in **9**, in cases where the choice is permitted (comp. § 102).

3. LIME FROM POTASSA AND SODA.

13 Precipitate the lime with oxalate of ammonia (§ 103, 2, *b*, *a*), evaporate the filtrate to dryness, and determine the alkalies in the ignited residue. In determining the alkalies, dissolve the residue, freed by ignition from the ammonia salts, in water, filter the solution from the undissolved portion, acidify the filtrate, according to circumstances, with hydrochloric acid or sulphuric acid, and then evaporate to dryness; this treatment of the residue is necessary, because oxalate of ammonia partially decomposes chlorides of the alkali metals upon ignition, and converts the bases into carbonates, except in presence of a large proportion of chloride of ammonium. The results are still more accurate than in **9**, except where oxalate of ammonia has been used, after the precipitation by carbonate of ammonia, to remove the minute traces of lime from the filtrate.

4. MAGNESIA FROM POTASSA AND SODA.†

a. Methods based upon the sparing solubility of Magnesia in Water.

14 α. Make a solution of the bases, as neutral as possible, and free from ammonia salts (it is a matter of indifference whether the acid is sulphuric, hydrochloric, or nitric), add baryta-water as long as a precipitate forms, heat to boiling, filter and wash the precipitate with boiling water. The precipitate contains the magnesia as hydrate; it is dissolved in hydrochloric acid, the baryta thrown down with sulphuric acid, and the magnesia as phosphate of magnesia and ammonia (§ 104, 2). The alkalies, which are contained in the solution, according to circumstances, as chlorides, nitrates, or caustic alkalies, are separated from the baryta as directed in **9** or **11**. The method gives good results, but is rather tedious.

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* This operation effects also the removal of the small quantity of sulphuric acid added to precipitate the traces of baryta, as sulphates of the alkalies are converted into chlorides of the alkali metals upon ignition in presence of a large proportion of chloride of ammonium.

† The methods α and β are suitable for the separation of magnesia from lithia.

β. Precipitate the solution with a little pure milk of lime, boil, filter, and wash. Separate the lime and the magnesia in the precipitate according to **25** or **29**; the lime and the alkalies in the filtrate, as directed in **9** or **13**. I am very fond of employing this method in cases where the magnesia has to be removed from a fluid containing lime and alkalies, provided the alkalies alone are to be determined. **15**

γ. Add to the chlorides pure oxalic acid in sufficient quantity to convert all the bases present, viewed as potassa, into quadroxalates; add some water, evaporate to dryness in a platinum dish, and ignite. By this operation the chlorides of the alkali metals are partially, the chloride of magnesium completely, converted into oxalates, which, upon ignition, give carbonated alkalies and magnesia. Treat the residue repeatedly with small quantities of boiling water; during this washing the precipitate may be transferred to the filter or remain in the dish, no matter which. When all the alkali salt is washed out, dry the filter, burn it in the dish, ignite strongly, and weigh the magnesia. If the solution looks a little turbid, evaporate to dryness, treat the residue with water, and filter off the trifling amount of magnesia still remaining; add, finally, hydrochloric acid to the filtrate, and determine the alkalies as chlorides. **16**

If the bases are present in form of sulphates, add to the boiling solution chloride of barium, until the formation of a precipitate just ceases, evaporate the filtrate with an excess of oxalic acid, and proceed as in **16**. Separate the carbonate of baryta, which remains mixed with magnesia, from the latter, as directed **22**. **17**

We owe these methods to Mitscherlich, and the description of them to Lasch.* I can add my own testimony to the accuracy of the results. Still the weighed alkali salt should always be tested with phosphate of soda and ammonia for magnesia. Usually a weighable precipitate is produced which cannot be passed over. **18**

The method described in **16** may also be successfully employed with nitrates, for which it is, indeed, specially recommended by Deville.† Carbonic acid and nitrous acid are evolved in the process of evaporation.

b. *Precipitation of Magnesia as Carbonate of Ammonia-Magnesia.*

Mix the solution of sulphates, nitrates, or chlorides (it must be very concentrated) with an excess of a concentrated solution of sesquicarbo- **19** nate of ammonia in water and ammonia (230 grm. of the salt, 180 c. c. solution of ammonia sp. gr. 0·92, and water to 1 litre). After twenty-four hours filter off the precipitate ($MgO, CO_2 + NH_4 O, CO_2 +$ 4 aq.), wash it with the solution of caustic and carbonated ammonia used for the precipitation, dry, ignite strongly and for a sufficient length of time, and weigh the magnesia. Evaporate the filtrate to dryness, keeping the heat at first under 100°, expel the ammonia salts, and determine the alkalies as chlorides or sulphates. When soda alone is present the results are satisfactory. In the presence of potassa the ignited magnesia must be extracted with water, before weighing, as it contains an appreciable quantity of carbonate of potassa; the washings are to be added to the principal filtrate. This last measure is unnecessary in the absence of potassa. Results satisfactory; the magnesia is a little too low. Mean error $\frac{9}{1000}$ (F. G. SCHAFFGOTSCH,* H. WEBER†).

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* Journ. f. prakt. Chem. 63, 343.

† Ibid. 60, 17.

II. SEPARATION OF THE OXIDES OF THE SECOND GROUP FROM EACH OTHER.

§ 154.

Index :—The Nos. refer to those in the margin.

Baryta from strontia, 21, 24, 32.
" lime, 21, 23, 24, 32.
" magnesia, 20, 22.
Strontia from baryta, 21, 24, 32.
" lime, 28, 31.
" magnesia, 20, 22,
Lime from baryta, 21, 23, 24, 32.
" strontia, 28, 31.
" magnesia, 20, 25, 26, 27, 29, 30.
Magnesia from baryta, 20, 22.
" strontia, 20, 22.
" lime, 20, 25, 26, 27, 29, 30.

A. *General Method.*

THE WHOLE OF THE ALKALINE EARTHS FROM EACH OTHER.

Proceed as in **9**. The magnesia is precipitated from the filtrate with phosphate of soda. The precipitated carbonates of the baryta, strontia, and lime, are dissolved in hydrochloric acid, and the bases separtaed as directed in **21**. The traces of magnesia, which may be present in the carbonate of ammonia precipitate, are obtained by evaporating the filtrate from the sulphate of strontia or lime to dryness, taking up the residue with water and precipitating the solution with phosphate of soda and ammonia. **20**

B. *Special Methods.*

1. *Methods based upon the Insolubility of Silicofluoride of Barium.*

BARYTA FROM STRONTIA AND FROM LIME.

Mix the neutral or slightly acid solution with hydrofluosilicic acid‡ **21** in excess, add a volume of spirit of wine equal or somewhat inferior to that of the fluid (H. ROSE), let the mixture stand twelve hours, collect the precipitate of *silicofluoride of barium* on a weighed filter, wash with a mixture of equal parts of water and spirit of wine, until the washings cease to show even the least trace of acid reaction (but no longer), and dry at 100°. Precipitate the strontia or lime from the filtrate by dilute sulphuric acid (§ 102, 1, *a*, and § 103, 1, *a*). The results are satisfactory. For the properties of silicofluoride of barium, see § 71. If both strontia and lime are present, the sulphates are weighed, converted into carbonates (§ 132, II., *b*), and the two bases then separated as directed in **31**.

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* Pogg. Annal. 104, 482.

† Vierteljahrsschrift f. prakt. Pharm. 8, 161.

‡ If not kept in a gutta-percha bottle it should be freshly prepared.

2. *Methods based upon the Insolubility of Sulphate of Baryta, or Sulphate of Strontia, as the case may be, in water and in Solution of Hyposulphite of Soda.*

a. BARYTA AND STRONTIA FROM MAGNESIA.

Precipitate the baryta and strontia with sulphuric acid (§ 101, 1, *a*, and § 102, 1, *a*), and the magnesia from the filtrate with phosphate of soda and ammonia (§ 104, 2). **22**

b. BARYTA FROM LIME.

Mix the solution with hydrochloric acid, then with highly dilute sulphuric acid (1 part acid to 300 water), as long as a precipitate forms; allow to deposit, and determine the sulphate of baryta as directed in § 101, 1, *a*. Concentrate the washings by evaporation, and add them to the filtrate, neutralize the acid with ammonia, and precipitate the lime as oxalate (§ 103, 2, *b*, *α*). The method is principally to be recommended when small quantities of baryta have to be separated from much lime. If we have to separate sulphate of lime from sulphate of baryta the salts may (in the absence of free acids) be treated repeatedly with a solution of hyposulphite of soda at a gentle heat. The sulphate of baryta remains undissolved, the sulphate of lime dissolves. The lime is precipitated from the filtrate by oxalate of ammonia (DIEHL[*]). **23**

3. *Method based upon the different deportment with Carbonated Alkalies of Sulphate of Baryta on the one hand, and Sulphates of Strontia and Lime on the other.*

BARYTA FROM STRONTIA AND LIME.

Digest the precipitated sulphates of the three bases for twelve hours, at the common temperature (15—20°), with frequent stirring, with a solution of carbonate of ammonia, decant the fluid on to a filter, treat the residue repeatedly in the same way, wash finally with water, and in the still moist precipitate, separate the undecomposed sulphate of baryta by means of cold dilute hydrochloric acid from the carbonates of strontia and lime formed. To hasten the separation you may boil the sulphates for some time with a solution of carbonate of potassa (not soda), to which ⅛ the amount of the car- **24**

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[*] Journ. f. prakt. Chem. 79, 30.

bonate, or more, of sulphate of po
process also the sulphates of stron
sulphate of baryta remaining unac
tion, the above solution of carbo
added in excess at once, and the wh
sisting of sulphate of baryta and c
to be treated as above with cold hy

4. *Method based on the Inso*
Alcohol.

[**Lime from Magnesia.**

a. Evaporate the hydrochloric
the residue with strong alcohol un
solution a slight excess of concentr
several hours. The precipitate, c
the magnesia as sulphates, is tra
strong, nearly absolute, alcohol an
washings cease to react acid to test
removed, continue the washing w
long as any solid matters are extra
filter and is weighed as sulphate,
filtrate and washings, from which,
it is thrown down as ammonio-p
Chizynski†).]

b. **Small quantities of Lime**
the bases into neutral sulphates, d
alcohol with constant stirring, till
produced. Wait a few hours and
sulphate of lime with alcohol, whic
volume of water, and determine it
the weighed sulphate must be test
precipitate in water containing hy
lime from the small quantity of m
according to **29** (Scheerer‡).

[*c.* In presence of phosphoric ac
acid solution to dryness, add strong a
rately strong sulphuric acid, and trea
as pure sulphate. The filtrate, afte
divided into two portions. In one
tion of chloride of ammonium, am
(§ 104, 2); from the other throw do
magnesia solution (§ 134, *b*, *α*).]

5. *Method based on the Insolub*
Solution of Sulphate of A

Strontia from Lime. If the mix
smallest quantity of water, add abou
substance of sulphate of ammonia di
of water, and either boil for some tim the water that
evaporates and addition of a very little ammonia (as the solution of
sulphate of ammonia becomes acid on boiling), or allow to stand at

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* Pogg. Annal. xcv. 286, 299, 427.

† Fres. Zeitschrift, iv. 348.

‡ Annal. d. Chem. u. Pharm. 110, 237.

the ordinary temperature for twelve hours. Filter and wash the precipitate, which consists of sulphate of strontia and a little sulphate of strontia and ammonia with a concentrated solution of sulphate of ammonia till the washings remain clear on addition of oxalate of ammonia. The precipitate is cautiously ignited, moistened with a little dilute sulphuric acid (to convert the small quantity of sulphide of strontium into sulphate), and weighed. The highly dilute filtrate is precipitated with oxalate of ammonia, and the lime determined according to § 103, 2, *b*, α. If you have the solid sulphates to analyze, they are very finely powdered and boiled with concentrated solution of sulphate of ammonia with renewal of the evaporated water and addition of a little ammonia. Results very close, *e.g.*, 1·048 SrO, NO_5 instead of 1·053, and 0·497 CaO, CO_2, instead of 0·504 (H. Rose*).

6. *Methods based upon the Insolubility of Oxalate of Lime in Chloride of Ammonium and in Acetic Acid.*

LIME FROM MAGNESIA.

a. Mix the properly diluted solution with sufficient chloride of ammonium to prevent the formation of a precipitate by ammonia, which is added in slight excess; and oxalate of ammonia as long as a precipitate forms, then a further portion of the same reagent, about sufficient to convert the magnesia also into oxalate (which remains in solution). This excess is absolutely indispensable to insure complete precipitation of the lime, as oxalate of lime is slightly soluble in solution of chloride of magnesium not mixed with oxalate of ammonia (Expt. No. 92). Let the mixture stand twelve hours in a moderately warm place, decant the supernatant clear fluid, as far as practicable, from the precipitated oxalate of lime, mixed with a little oxalate of magnesia, on to a filter, wash the precipitate once in the same way by decantation, then dissolve in hydrochloric acid, add water, then ammonia in slight excess, and a little oxalate of ammonia. Let the fluid stand until the precipitate has completely subsided, then pour on to the previous filter, transfer the precipitate finally to the latter, and proceed exactly as directed § 103, 2, *b*, α. The first filtrate contains the larger portion of the magnesia, the second the remainder. Evaporate the second filtrate, acidified with hydrochloric acid, to a small volume, then mix the two fluids, and precipitate the magnesia with phosphate of soda as directed § 104, 2. If the quantity of ammonia salts present is considerable, the estimation of the magnesia is rendered more accurate by evaporating the fluids, in a large platinum or silver dish,† to dryness, and igniting the residuary saline mass, in small portions at a time, in a smaller platinum dish, until the ammonia salts are expelled. The residue is then treated with hydrochloric acid and water, heat applied, the fluid filtered ‡ and finally precipitated with ammonia and phosphate of soda. 29

Numerous experiments have convinced me that this method, which is so frequently employed, gives accurate results only if the foregoing instructions are strictly complied with. It is only in cases where the bonate, or more, of sulphate of potassa has been added. By this process also the sulphates of strontia and lime are decomposed, the sulphate of baryta remaining unacted on. If the bases are in solution, the above solution of carbonate and sulphate of potassa is added in excess at once, and the whole boiled. The precipitate, consisting of sulphate of baryta and carbonates of strontia and lime, is to be treated as above with cold hydrochloric acid (H. ROSE [*]).

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* Pogg. Annal. 110, 296.

† A porcelain dish does not answer so well (see Expt. No. 3).

‡ If the process of evaporation has been conducted in a silver vessel, a little chloride of silver will often separate.

4. *Method based on the Insolubility of Sulphate of Lime in Alcohol.*

[LIME FROM MAGNESIA.

a. Evaporate the hydrochloric solution nearly to dryness, treat **25** the residue with strong alcohol until it is dissolved. Add to the solution a slight excess of concentrated sulphuric acid and let stand several hours. The precipitate, containing all the lime and some of the magnesia as sulphates, is transferred to a filter with the aid of strong, nearly absolute, alcohol and washed with the same until the washings cease to react acid to test paper. After all free acid is thus removed, continue the washing with alcohol of 35—40 per cent. as long as any solid matters are extracted. The lime all remains on the filter and is weighed as sulphate, the magnesia is all found in the filtrate and washings, from which, after evaporating off the alcohol, it is thrown down as ammonio-phosphate. Excellent method (A. CHIZYNSKI [†]).]

b. SMALL QUANTITIES OF LIME FROM MUCH MAGNESIA. Convert **26** the bases into neutral sulphates, dissolve the mass in water, and add alcohol with constant stirring, till a slight permanent turbidity is produced. Wait a few hours and then filter, wash the precipitated sulphate of lime with alcohol, which has been diluted with an equal volume of water, and determine it after § 103, 1, *a* (in which case the weighed sulphate must be tested for magnesia), or dissolve the precipitate in water containing hydrochloric acid and separate the lime from the small quantity of magnesia possibly coprecipitated according to **29** (SCHEERER [‡]).

[*c.* In presence of phosphoric acid, evaporate the hydrochloric **27** acid solution to dryness, add strong alcohol to the residue, then moderately strong sulphuric acid, and treat as in *a.* The lime is separated as pure sulphate. The filtrate, after evaporating of the alcohol, is divided into two portions. In one magnesia is precipitated by addition of chloride of ammonium, ammonia, and phosphate of soda (§ 104, 2); from the other throw down phosphoric acid by means of magnesia solution (§ 134, *b*, α).]

5. *Method based on the Insolubility of Sulphate of Strontia in Solution of Sulphate of Ammonia.*

STRONTIA FROM LIME. If the mixture is soluble, dissolve in the **28** smallest quantity of water, add about 50 times the quantity of the substance of sulphate of ammonia dissolved in four times its weight of water, and either boil for some time with renewal of the water that evaporates and addition of a very little ammonia (as the solution of sulphate of ammonia becomes acid on boiling), or allow to stand at the ordinary temperature for twelve hours. Filter and wash the precipitate, which consists of sulphate of strontia and a little sulphate of strontia and ammonia with a concentrated solution of sulphate of ammonia till the washings remain clear on addition of oxalate of ammonia. The precipitate is cautiously ignited, moistened with a little dilute sulphuric acid (to convert the small quantity of sulphide of strontium into sulphate), and weighed. The highly dilute filtrate is precipitated with oxalate of ammonia, and the lime determined according to § 103, 2, *b*, α. If you have the solid sulphates to analyze, they are very finely powdered and boiled with concentrated solution of sulphate of ammonia with renewal of the evaporated water and addition of a little ammonia. Results very close, *e.g.*, 1·048 SrO, NO_5 instead of 1·053, and 0·497 CaO, CO_2, instead of 0·504 (H. Rose*).

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[*] Pogg. Annal. xcv. 286, 299, 427.

[†] Fres. Zeitschrift, iv. 348.

[‡] Annal. d. Chem. u. Pharm. 110, 237.

6. *Methods based upon the Insolubility of Oxalate of Lime in Chloride of Ammonium and in Acetic Acid.*

LIME FROM MAGNESIA.

a. Mix the properly diluted solution with sufficient chloride of ammonium to prevent the formation of a precipitate by ammonia, which is added in slight excess; and oxalate of ammonia as long as a precipitate forms, then a further portion of the same reagent, about sufficient to convert the magnesia also into oxalate (which remains in solution). This excess is absolutely indispensable to insure complete precipitation of the lime, as oxalate of lime is slightly soluble in solution of chloride of magnesium not mixed with oxalate of ammonia (Expt. No. 92). Let the mixture stand twelve hours in a moderately warm place, decant the supernatant clear fluid, as far as practicable, from the precipitated oxalate of lime, mixed with a little oxalate of magnesia, on to a filter, wash the precipitate once in the same way by decantation, then dissolve in hydrochloric acid, add water, then ammonia in slight excess, and a little oxalate of ammonia. Let the fluid stand until the precipitate has completely subsided, then pour on to the previous filter, transfer the precipitate finally to the latter, and proceed exactly as directed § 103, 2, *b*, α. The first filtrate contains the larger portion of the magnesia, the second the remainder. Evaporate the second filtrate, acidified with hydrochloric acid, to a small volume, then mix the two fluids, and precipitate the magnesia with phosphate of soda as directed § 104, 2. If the quantity of ammonia salts present is considerable, the estimation of the magnesia is rendered more accurate by evaporating the fluids, in a large platinum or silver dish,† to dryness, and igniting the residuary saline mass, in small portions at a time, in a smaller platinum dish, until the ammonia salts are expelled. The residue is then treated with hydrochloric acid and water, heat applied, the fluid filtered ‡ and finally precipitated with ammonia and phosphate of soda. **29**

Numerous experiments have convinced me that this method, which is so frequently employed, gives accurate results only if the foregoing instructions are strictly complied with. It is only in cases where the quantity of magnesia present is relatively small, that a single precipitation with oxalate of ammonia may be found sufficient (comp. Expt. No. 93).

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* Pogg. Annal. 110, 296.

† A porcelain dish does not answer so well (see Expt. No. 3).

‡ If the process of evaporation has been conducted in a silver vessel, a little chloride of silver will often separate.

30 *b.* In the case of lime and magnesia combined with phosphoric acid, dissolve in the least possible quantity of hydrochloric acid, add ammonia until a copious precipitate forms; redissolve this by addition of acetic acid, and precipitate the lime from the solution with an excess of oxalate of ammonia. To determine the magnesia, precipitate the filtrate with ammonia and phosphate of soda. As free acetic acid by no means prevents the precipitation of small quantities of oxalate of magnesia, the precipitate contains some magnesia, and, as oxalate of lime is not quite insoluble in acetic acid, the filtrate contains some lime; these two sources of error compensate each other in some measure. In accurate analyses, however, these trifling admixtures of magnesia and lime are afterwards separated from the weighed precipitates of carbonate of lime and pyrophosphate of magnesia respectively.

7. *Indirect Method.*

STRONTIA FROM LIME.

31 Determine both bases first as carbonates, precipitating them either with carbonate or with oxalate of ammonia (§§ 102, 103); then estimate the amount of carbonic acid in them, and calculate the amount of strontia and of lime as directed in § 197. The determination of the carbonic acid may be effected by fusion with vitrified borax (§ 139, II., *c*), but the application of a moderate white heat, such as is given by a good gas blast-lamp without the use of a crucible jacket, is alone sufficient to drive out all the carbonic acid from both the carbonates (F. G. SCHAFFGOTSCH *). I can strongly recommend this method. It is well to precipitate the carbonates hot, to press the precipitate cautiously down in the platinum crucible and turn over the agglomerated cake every now and then till, after repeated ignitions, the weight has become constant. The results are good, if neither of the bases is present in too minute quantity.

32 The indirect separation may of course be effected by means of other salts, and can be used also for the determination of LIME IN PRESENCE OF BARYTA or of BARYTA IN PRESENCE OF STRONTIA. In the expulsion of carbonic acid from carbonate of baryta vitrified borax must be used (§ 139, II., *c*).

THIRD GROUP.

ALUMINA—SESQUIOXIDE OF CHROMIUM.

I. SEPARATION OF THE OXIDES OF THE THIRD GROUP FROM THE ALKALIES.

§ 155.

1. FROM AMMONIA.

33 *a.* Salts of alumina and of sesquioxide of chromium may be separated from salts of ammonia by ignition. However, in the

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* Pogg. Annal. 113, 615.

case of alumina, this method is applicable only in the absence of chlorine (volatilization of chloride of aluminium). The safest way, therefore, is to mix the compound with carbonate of soda before igniting.

b. Determine the ammonia by one of the methods given in § 99, 3, **34** using solution of potassa or soda to effect the expulsion of the ammonia. The alumina and sesquioxide of chromium are then determined in the residue in the same way as in **35**.

2. FROM POTASSA AND SODA.

a. Precipitate and determine the sesquioxide of chromium and **35** alumina as directed in § 105, *a*, and § 106, *a*. The filtrate contains the alkalies, which are then freed from the salt of ammonia formed, by evaporation to dryness and ignition.

b. *Alumina* may be separated also from potassa and soda, by heat- **36** ing the nitrates (see **38**).

II. SEPARATION OF THE OXIDES OF THE THIRD GROUP FROM THE ALKALINE EARTHS.

§ 156.

Index:—The Nos. refer to those in the margin.
Alumina from baryta, 37, 42, 43.
" strontia, 37, 42, 43.
" lime, 37, 42, 44, 45, 46.
" magnesia, 37, 42, 45, 46.
Sesquioxide of chromium from the alkaline earths, 47, 48.

SEPARATION OF ALUMINA FROM THE ALKALINE EARTHS.

A. *General Methods.*

THE WHOLE OF THE ALKALINE EARTHS FROM ALUMINA.

1. *Precipitation of Alumina by Ammonia, and its Solution in Soda.*

Mix the moderately dilute hot solution (preferably in a platinum **37** dish) with a tolerable quantity of chloride of ammonium, if such be not already present, add ammonia in moderate excess, and boil till no more free ammonia is observable. Under these circumstances, a little magnesia, and also a small quantity of carbonate of lime, baryta, or strontia are at first precipitated along with the alumina; on the boiling with chloride of ammonium, the coprecipitated alkaline earths redissolve, so that the alumina finally retains only an unweighable or scarcely weighable trace of magnesia. Allow to deposit, and proceed with the alumina determination according to § 105, *a*. After it has been weighed fuse it for a long time with bisulphate of potassa, dissolve the fused mass in water, and determine any silicic acid * that may remain. The solution, when mixed with potassa in excess, will not appear perfectly clear, but will contain a few flocks of magnesia. If there is any amount of the latter, filter it off, dissolve in nitric acid, precipitate with ammonia, boil till the fluid ceases to smell of ammonia, filter, evaporate the small quantity of fluid in a platinum capsule, ignite, weigh the residual magnesia, deduct it from the alumina and add it, on the other hand, to the principal quantity of the magnesia. In order to the further separation of the alkaline earths, acidify the fluid containing them with hydrochloric acid, evaporate (preferably in a platinum dish) to a small bulk, and while still warm add ammonia just in excess. A small precipitate of alumina is sometimes formed at this stage; filter off, wash and weigh with the principal precipitate. In the filtrate determine the alkaline earths according to § 154.

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* A small quantity will always be found if you have boiled in a glass or porcelain vessel.

2. *Unequal Decomposability of the Nitrates at a Moderate Heat* (DEVILLE*).

To make this simple and convenient method applicable, the bases **38** must be present as pure nitrates. Evaporate to dryness in a platinum dish, and heat gradually, with the cover on, in the sand- or air-bath—or, better still, on a thick iron disk, with two cavities, one for the platinum dish, the other, filled with brass filings, for the thermometer—to from 200° to 250°, until a glass rod moistened with ammonia ceases to indicate further evolution of nitric acid fumes. You may also, without risk, continue to heat until nitrous acid vapors form. The residue consists of alumina, nitrates of baryta, strontia, and lime, and nitrate and basic nitrate of magnesia.

Moisten the mass with a concentrated solution of nitrate of ammonia, and heat gently, but do not evaporate to dryness. Repeat this operation until no further evolution of ammonia is perceptible. (The basic nitrate of magnesia, insoluble in water, dissolves in nitrate of ammonia, with evolution of ammonia, as neutral nitrate of magnesia.) Add water, and digest at a gentle heat.

> If the nitrate of ammonia has evolved only imperceptible traces of ammonia, pour hot water into the dish, stir, and add a drop of dilute ammonia; this must cause no turbidity in the fluid; should the fluid become turbid, this proves that the heating of the nitrates has not been continued long enough; in which case you must again evaporate the contents of the dish, and heat once more.

The alumina remains undissolved in the form of a dense granular substance. Decant after digestion, and wash with boiling water; ignite strongly in the same vessel in which the separation has been effected, and weigh. Separate the alkaline earths as directed § 154.

In the same way alumina may be separated also from potassa and soda.

3. *Method in which the processes of* 1 *and* 2 *are combined.*

Precipitate the alumina as in **37**, wash in the same way as there **39** directed, then treat while still moist with nitric acid, and proceed according to **38** to remove the trifling amount of magnesia, &c., coprecipitated; add the solution obtained to the principal solution of the alkaline earths, and treat the fluid as directed in **37**. This method may be employed also in the case of chlorides; it will be sometimes found useful.

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* Journ. f. prakt. Chem. 1853, 60, 9.

4. *Precipitation of Alumina by Acetate or Formiate of Soda upon boiling.*

40 The same process as for the separation of sesquioxide of iron from the alkaline earths. The method is employed more particularly when both alumina and sesquioxide of iron have to be separated from alkaline earths at the same time (§ 113, 1, d).

5. *Precipitation of Alumina by Succinate of Ammonia.*

41 Proceed as for the precipitation of sesquioxide of iron by the same reagent (§ 113, 1, *c*); especially to be employed, when alumina and sesquoixide of iron are both to be separated from alkaline earths at the same time.

B. *Special Methods.*

SOME OF THE ALKALINE EARTHS FROM ALUMINA.

1. *Precipitation of some of the Salts of the Alkaline Earths.*

a. BARYTA AND STRONTIA FROM ALUMINA.

43 Precipitate the baryta and strontia with *sulphuric acid* (§§ 101 and 102), and the alumina from the filtrate as directed § 105, *a*. This method is especially suited for the separation of baryta from alumina.

b. LIME FROM ALUMINA.

44 Add ammonia to the solution until a permanent precipitate forms, then acetic acid until this precipitate is redissolved, then acetate of ammonia, and finally *oxalate of ammonia* in slight excess (§ 103, 2, *b*, β); allow the precipitated oxalate of lime to deposit in the cold, then filter, and precipitate the alumina from the filtrate as directed § 105, *a*. In presence of oxalate of ammonia, alumina requires some time for precipitation (PISANI).

c. MAGNESIA AND SMALL QUANTITIES OF LIME FROM ALUMINA.

45 Mix with some tartaric acid, supersaturate with ammonia and from the clear fluid (in the presence of enough alumina no tartrate of lime is precipitated) precipitate first the lime by oxalate of ammonia, then the magnesia by phosphate of soda. If the alumina is to be determined in the filtrate, the latter must be evaporated with addition of carbonate of soda and nitre to dryness, the residue ignited, softened with water, dissolved in hydrochloric acid (not in the platinum dish), and the alumina precipitated by ammonia. The ammonio-phosphate of magnesia which may contain basic tartrate of magnesia is to be dissolved in hydrochloric acid, reprecipitated with ammonia, then dried and weighed. [Not applicable when alumina is present in large proportion, since alumina salts dissolve ammonio-phosphate of magnesia (KNAPP).]

2. *Precipitation of Alumina by Carbonate of Baryta.*

ALUMINA FROM MAGNESIA, AND SMALL QUANTITIES OF LIME.

46 Mix the slightly acid dilute fluid in a flask, with carbonate of baryta (shaken up with water), in moderate excess; cork the flask and let the mixture stand in the cold until the hydrated alumina has subsided, wash by decantation three times, filter, and then determine the alumina in the precipitate as directed 43; in the filtrate, first precipitate the baryta by sulphuric acid (**23**), and then separate the lime and magnesia according to § 154.

SEPARATION OF SESQUIOXIDE OF CHROMIUM FROM THE ALKALINE EARTHS.

The best way to effect the separation of sesquioxide of chromium from the alkaline earths at the same time, is to convert the sesquioxide into chromic acid. For this purpose the pulverized substance is mixed with 2½ parts of pure *carbonate of soda* and 2½ parts of *nitrate of potassa*, and the mixture heated in a platinum crucible to fusion. On treating the fused mass with hot water, the chromium dissolves as alkaline chromate; the residue contains the alkaline earths as carbonates, or in the caustic state (magnesia). The chromium in the solution is determined as directed § 130. **47**

I need hardly observe that sesquioxide of chromium may also be separated from *baryta* and, though less perfectly, from *strontia*, by means of *sulphuric acid* added to the acid solution of the substance. Sesquioxide of chromium cannot be separated by ammonia from the alkaline earths, since, even though carbonic acid be completely excluded, particles of the alkaline earths are thrown down with the sesquioxide of chromium. From solutions containing a salt of sesquioxide of chromium, lime cannot be precipitated completely by oxalate of ammonia; but it may be by sulphuric acid and alcohol (§ 103, 1). **48**

III. SEPARATION OF SESQUIOXIDE OF CHROMIUM FROM ALUMINA.

§ 157.

a. Fuse the oxides with 2 parts by weight of nitrate of potassa and 4 parts of carbonate of soda, in a platinum crucible, treat the fused mass with boiling water, rinse the contents of the crucible into a porcelain dish or beaker, add a somewhat large quantity of chlorate of potassa, supersaturate slightly with hydrochloric acid, evaporate to the consistence of syrup, and add, during the latter process, some more chlorate of potassa in portions, to remove the free hydrochloric acid. Dilute now with water, and precipitate the alumina by carbonate of ammonia or ammonia as directed in § 105, *a*. The alumina falls down free from sesquioxide of chromium. In the filtrate the chromium is determined as directed § 130. If you omit the evaporation with hydrochloric acid and chlorate of potassa, part of the chromic will be reduced by the nitrous acid in the fluid, and sesquioxide of chromium will accordingly, upon addition of ammonia, precipitate with the alumina (DEXTER*). **49**

b. Dissolve the oxides in hydrochloric acid [make the solution nearly neutral by carbonate of soda, add acetate of soda in excess], and saturate the solution with chlorine gas. The sesquioxide of chromium will be converted into chromic acid, and the alumina partially separated. When the fluid has become of a pure yellow color, heat to remove the excess of chlorine, add carbonate of ammonia, and digest to destroy the hypochlorous acid and precipitate the still dissolved alumina, filter off the alumina, and determine it according to § 105, **50**

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* Pogg. Annal. 89, 142.

a. In the fluid the chromium is determined according to § 130, I., *a.* (Wöhler,[*] [Gibbs][†]).

FOURTH GROUP.

OXIDE OF ZINC—PROTOXIDE OF MANGANESE—PROTOXIDE OF NICKEL—PROTOXIDE OF COBALT—PROTOXIDE OF IRON—SESQUIOXIDE OF IRON—(SESQUIOXIDE OF URANIUM).

I. Separation of the Oxides of the Fourth Group from the Alkalies.

§ 158.

A. *General Methods.*

1. All the Oxides of the Fourth Group from Ammonia.

Proceed as for the separation of sesquioxide of chromium and alumina from ammonia, **33**. It must be borne in mind that the oxides of the fourth group comport themselves, upon ignition with chloride of ammonium, as follows: Sesquioxide of iron is partly volatilized as sesquichloride; the oxides of manganese are converted into protochloride of manganese, containing protosesquioxide of that metal; the oxides of nickel and cobalt are reduced to the metallic state; oxide of zinc volatilizes, with access of air, as chloride of zinc (H. Rose). It is, therefore, generally the safest way to add carbonate of soda. The ammonia is determined in a separate portion. **51**

2. All Oxides of the Fourth Group from Potassa and Soda.

Mix the solution in a flask with chloride of ammonium if necessary, add ammonia till neutral or slightly alkaline, then yellow sulphide of ammonium saturated with sulphuretted hydrogen, fill the flask nearly to the top with water, cork it, allow the precipitated sulphides to subside, and then filter them off from the fluid containing the alkalies. In performing this process the precautionary rules given under the heads of the several metals in question (§§ 108—113) must be borne in mind.[‡] (If notwithstanding, the filtrate is brownish, acidify it with acetic acid, boil and filter off the small quantity of the sulphide of nickel which then separates.) Acidify the filtrate with hydrochloric acid, evaporate, filter off the sulphur, if necessary, continue the evaporation to dryness, ignite the residue to remove the ammonia salts, and determine the alkalies by the methods given §152. **52**

B. *Special Methods.*

1. Oxide of Zinc from Potassa and Soda, by precipitating the zinc from the solution of the acetates with sulphuretted hydrogen (see p. 181 and **72**). **53**

2. Sesquioxide of Iron from Potassa and Soda, by precipitating the sesquioxide of iron with ammonia; or by heating the nitrates (see **38**).

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[*] Annal. d. Chem. u. Pharm. 106, 121.

[†] Am. Jour. Science, 2d ser. 39, 59.

[‡] Nickel and cobalt may be separated from the alkalies also in the manner given in **73**

3. Protoxide of Manganese from the Alkalies.

a. Saturate the solution with *chlorine*, and precipitate the manganese—as hydrated sesquioxide—with carbonate of baryta or ammonia. The latter precipitant is apt to leave some manganese in solution [see also **61**]. **54**

b. Heat the nitrates (Deville); (see **62**).

II. Separation of the Oxides of the Fourth Group from the Alkaline Earths.

§ 159.

Index :—The Nos. refer to those in the margin.

Oxide of zinc from baryta, strontia, and lime, 55, 56, 57, 63.
" magnesia, 55, 57.
Protoxide of manganese from baryta, strontia, and lime, 55, 56, 59—62—67.
Protoxide of manganese from magnesia, 55, 59, 62.
Protoxides of nickel and cobalt from baryta, strontia, and lime, 55, 56, 63.
" magnesia, 55.
Sesquioxide of iron from baryta, strontia, and lime, 55, 56, 58.
" magnesia, 55, 58.

A. *General Method.*

All Oxides of the Fourth Group from the Alkaline Earths.

55 Add to the solution chloride of ammonium, and, if acid, also ammonia, and precipitate with sulphide of ammonium, as in **52**. Take care to use slightly yellow sulphide of ammonium, perfectly saturated with sulphuretted hydrogen, and free from carbonate and sulphate of ammonia, and to employ it in sufficient excess. Insert the cork, and let the flask stand for some time, to allow the precipitate to subside, then wash quickly, and as far as practicable, out of the contact of air, with water to which some sulphide of ammonium has been added. Acidify the filtrate with hydrochloric acid, heat, filter from the sulphur, and separate the alkaline earths, as directed in § 154. If the filtrate is brownish from a little dissolved sulphide of nickel, acidify it with acetic acid instead of with hydrochloric acid, boil, and filter.

If the quantity of the alkaline earths is rather considerable, it is advisable to treat the slightly washed precipitate once more with hydrochloric acid (in presence of nickel or cobalt, it is not necessary to effect complete solution), heat the solution gently for some time, and then reprecipitate in the same way.

If we have merely to effect the removal of nickel and cobalt, we may also, after addition of sulphide of ammonium, acidify with acetic acid, and filter. Cobalt alone may be separated as follows: after precipitating the ammoniacal solution with sulphide of ammonium, boil the whole till the free ammonia has escaped, add a few drops of sulphide of ammonium and ammonia, and filter (H. Rose*).

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* Pogg. Annal. 110, 416.

B. *Special Methods.*

1. BARYTA, STRONTIA, AND LIME, FROM THE WHOLE OF THE OXIDES OF THE FOURTH GROUP.

Precipitate the baryta and strontia from the acid solution **56**
with sulphuric acid (§§ 101 and 102), in the presence of lime add $\frac{1}{6}$—$\frac{1}{8}$ volume of strong alcohol (§ 103). For baryta this method is preferable to all others.

2. OXIDE OF ZINC FROM THE ALKALINE EARTHS.

Convert the bases into acetates, and precipitate the zinc from **57**
the solution as directed in § 108, 1, *b*.

3. SESQUIOXIDE OF IRON FROM THE ALKALINE EARTHS.

a. Mix the somewhat acid solution with enough chloride **58**
of ammonium, heat to boiling, add slight excess of ammonia, boil, till the excess of the latter is expelled, and filter. The solution is free from iron, the precipitate is free from lime, baryta, and strontia, but contains a very slight trace of magnesia (H. ROSE*).

b. Precipitate the sesquioxide of iron as basic acetate or formiate (§ 113, 1, *d* [and § 81, *e*]). The method is good and can frequently be employed.

c. Decompose the nitrates by heat (**38**).

4. PROTOXIDE OF MANGANESE FROM THE ALKALINE EARTHS.

Separation of Manganese as Sesquioxide or Binoxide.

α. SCHIEL'S Method.†—Add to the hydrochloric acid solution car- **59**
bonate of soda until the fluid is nearly neutralized, mix with acetate of soda, dilute sufficiently, and then conduct *chlorine gas* into the mixture. The acetate of protoxide of manganese is decomposed, and the whole of the manganese separates as binoxide. The alkaline earths remain in solution. The solution is kept heated to between 50° and 60°, whilst the chlorine gas is transmitted through it; as soon as the binoxide has separated, the transmission of the gas is stopped. The protosesquioxide of manganese obtained by the ignition of the binoxide so produced contains alkali. The binoxide must therefore be dissolved in hydrochloric acid, and the solution precipitated as directed § 109, 3. Instead of chlorine gas, solution of hypochlorous acid or of hypochlorite of soda may be used.‡ In using the latter, care must be taken to keep the fluid always slightly acid by acetic acid. The method is good.

β. H. ROSE‖ recommends to mix the dilute solution with acetate **60**
of soda, heat and saturate with chlorine gas, then to the fluid, which becomes red from the formation of permanganic acid, to add excess of ammonia (in presence of much magnesia, also chloride of ammoni-

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* Pogg. Annal. 110, 300.

† Sillim. Journ. 15, 275.

‡ [Bromine is the most convenient reagent to employ for the above purpose.]

‖ Pogg. Annal. 110, 305.

um), to boil, till all free ammonia is expelled, and filter off the precipitated sesquioxide of manganese. The manganese may also be completely precipitated from a dilute cold fluid saturated with chlorine by means of carbonate of baryta.

[γ. REICHARDT* directs to add to the hot and dilute hydrochlor- **61**
ic acid solution carbonate of soda until a slight permanent precipitate is formed, to redissolve this by the least necessary hydrochloric acid, and to add excess of (crystals of) acetate of soda. The acetic solution thus obtained is heated just to boiling, and solution of hypochlorite of soda (procured by boiling good bleaching powder with solution of carbonate of soda, using the latter in but slight excess) is added in sufficient quantity with stirring. That enough hypochlorite has been added is shown by the reddening and subsequent bleaching of litmus paper. This test should not be applied until the hypochlorite has had a little time to react on the manganese. If the acetic acid should be neutralized more must be added. After a few minutes filter and wash with hot water. Reichardt assures that the binoxide thus obtained is free from alkali.]

δ. DEVILLE'S Method.†—The bases must be present as nitrates. **62**
Heat in a covered platinum dish to from 200° to 250°, until the formation of fumes has completely ceased, and the mass has become black; and proceed in all other respects as directed in **38**. The presence of a small quantity of organic matter, or the action of a too intense heat, may cause the reduction of traces of binoxide of manganese, and their solution in nitrate of ammonia; these traces will be found with the magnesia.

5. PROTOXIDE OF COBALT, PROTOXIDE OF NICKEL, AND OXIDE OF ZINC, FROM BARYTA, STRONTIA, AND LIME.

Mix with carbonate of soda in excess, add cyanide of potassium, **63**
heat very gently, until the precipitated carbonates of protoxide of cobalt, protoxide of nickel, and oxide of zinc are redissolved; then filter the alkaline earthy carbonates from the solution of the cyanides in cyanide of potassium. The former are dissolved in dilute hydrochloric acid, and separated according to § 154; the latter are separated according to § 160.

III. SEPARATION OF THE OXIDES OF THE FOURTH GROUP FROM THOSE OF THE THIRD, AND FROM EACH OTHER.

§ 160.

Index:—The Nos. refer to those in the margin.

Alumina from oxide of zinc, 64, 65, 70, 71, 81.
" protoxide of manganese, 64. 65, 66, 68, 70, 71, 78.
" protoxides of nickel and cobalt, 64, 65, 67, 70, 71, 81.
" protoxide of iron, 64. 65, 66, 67.
" sesquioxide of iron, 65, 66, 67, 75, 84.
Sesquioxide of chromium from oxide of zinc, protoxides of manganese, nickel, cobalt, and iron, 64, 65, 76.
" sesquioxide of iron, 65, 75, 76.
Analysis of chromic iron, 77.

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[*] Fres. Zeitschrift, v. 62.

[†] Journ. f. prakt. Chem. 60, 11

Oxide of zinc from alumina, 64, 65, 70, 71, 81.
" protoxide of manganese, 64, 65, 76, 78.
" protoxide of nickel, 74, 83.
" protoxide of cobalt, 72, 74, 79.
" sesquioxide of iron, 64, 69, 70, 71, 85.
Protoxide of manganese from alumina, 64, 65, 66, 68, 70, 71, 78.
" sesquioxide of chromium, 64, 65, 76.
" oxide of zinc, 78.
" protoxide of nickel, 73, 74, 78, 80.
" protoxide of cobalt, 73, 74, 79, 80.
" sesquioxide of iron, 64, 68, 69, 70, 71.
Protoxide of nickel from alumina, 64, 65, 67, 70, 71, 81.
" sesquioxide of chromium, 64, 65, 76.
" oxide of zinc, 72, 74, 83.
" protoxide of manganese, 73, 74, 78, 80.
" protoxide of cobalt, 79, 82.
" sesquioxide of iron, 64, 69, 70, 71, 73, 85.
Protoxide of cobalt from alumina, 64, 65, 67, 70, 71, 81.
" sesquioxide of chromium, 64, 65, 76.
" oxide of zinc, 72, 74, 79.
" protoxide of manganese, 73, 74, 79, 80.
" protoxide of nickel, 79, 82.
" sesquioxide of iron, 64, 69, 70, 71, 73.
Protoxide of iron from alumina, 64, 65, 66, 67.
" sesquioxide of chromium, 64, 65, 76.
" sesquioxide of iron, 64, 85.
Sesquioxide of iron from alumina, 66, 67, 75, 84.
" sesquioxide of chromium, 65, 75, 76.
" oxide of zinc, 64, 69, 70, 71, 85.
" protoxide of manganese, 64, 68, 69, 70, 71.
" protoxide of nickel, 64, 69, 70, 71, 73, 85.
" protoxide of cobalt, 64, 69, 70, 71, 73.
" protoxide of iron, 64, 85.

A. *General Methods.*

1. *Precipitation of some Oxides by Carbonate of Baryta.*

SESQUIOXIDE OF IRON, ALUMINA, AND SESQUIOXIDE OF CHROMIUM, FROM ALL OTHER BASES OF THE FOURTH GROUP.

64 Mix the sufficiently dilute solution of the chlorides or nitrates, but not sulphates, which must contain a little free acid,[*] in a flask, with a moderate excess of carbonate of baryta diffused in water; cork, and allow to stand some time in the cold, with occasional shaking. The sesquioxide of iron, alumina, and sesquioxide of chromium, are completely separated,[†] whilst the other bases remain in solution, with the exception perhaps of traces of protoxide of cobalt and protoxide of nickel, which will generally fall down with the precipitated oxides. This may be prevented, at least as regards nickel, by addition of chloride of ammonium to the fluid to be precipitated (SCHWARZENBERG[‡]). Decant, stir up with cold water, allow to deposit, decant again, filter, and wash with cold water. The precipitate contains, besides the precipitated oxides, carbonate of baryta; and the filtrate, besides the non-precipitated oxides, a salt of baryta.

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[*] If there is much free acid, the greater part of it must first be saturated with carbonate of soda.

[†] The separation of the sesquioxide of chromium requires the most time.

[‡] Annal. d. Chem. u. Pharm. 97, 216.

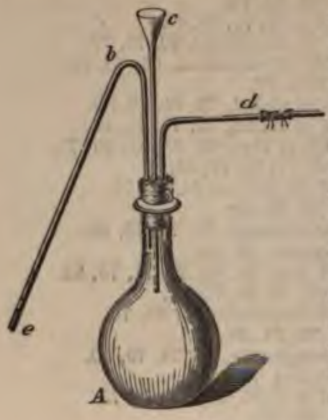

Fig. 66.

If protoxide of iron is present, and it is wished to separate it by this method from sesquioxide of iron, &c., the air must be excluded during the whole of the operation. In that case, the solution of the substance, the precipitation, and the washing by decantation, are effected in a flask (*A*, fig. 66), through which carbonic acid is transmitted (*d*). The washing water, boiled free from air, and cooled out of contact of air (preferably in a current of carbonic acid), is poured in through a funnel tube (*c*), and the fluid drawn off by means of a movable syphon (*b*); all the tubes are fitted air-tight into the cork; they are smeared with tallow.

2. *Precipitation of the Oxides of the Fourth Group, by Sulphide of Sodium, or Sulphide of Ammonium, from Alkaline Solution effected with the aid of Tartaric Acid.*

ALUMINA AND SESQUIOXIDE OF CHROMIUM FROM THE OXIDES OF THE FOURTH GROUP.

Mix the solution with tartaric acid, then with pure solution of soda or potassa until the fluid has cleared again;* add sulphide of sodium as long as a precipitate forms, allow it to deposit until the supernatant fluid no longer exhibits a greenish or brownish tint; decant, stir the precipitate up with water containing sulphide of sodium, decant again, transfer the precipitate, which contains all the metals of the fourth group, to a filter, wash with water containing sulphide of sodium, and separate the metals as directed in B. Add to the filtrate nitrate of potassa, and evaporate to dryness; fuse the residue, and separate the alumina from the chromic acid formed, as directed § 157. If you have merely to separate alumina from the oxides of the fourth group, it is better, after addition of tartaric acid, to supersaturate with ammonia, add chloride of ammonium, and precipitate in a flask with sulphide of ammonium. When the precipitate has settled it is filtered off and washed with water containing sulphide of ammonium. The filtrate is evaporated with addition of carbonate of soda and nitrate of potassa to dryness, fused, and the alumina determined in the residue. **65**

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* Sesquioxide of chromium and oxide of zinc cannot be obtained together in alkaline solution (Chancel, Compt. rend. 43, 927; Journ. f. prakt. Chem. 70, 378).

B. *Special Methods.*

1. *Solubility of Alumina in Caustic Alkalies.*

a. ALUMINA FROM PROTOXIDE AND SESQUIOXIDE OF IRON, AND SMALL QUANTITIES OF PROTOXIDE OF MANGANESE (but not from the protoxides of nickel and cobalt).

Heat the rather concentrated acid solution in a flask to boiling, remove from the gas, and reduce the sesquioxide of iron present by sulphite of soda. Replace the fluid over the lamp, keep boiling some time, and then neutralize with carbonate of soda, add solution of pure soda or potassa in excess, and boil for some time. **66**

If the analyzed substance contains much iron, the precipitate will become black and granular, which is a proof that the iron has been converted into protosesquioxide. The tendency to bumping, preceding the actual ebullition of the fluid, may be guarded against by means of a spiral coil of platinum wire placed in the liquid, or by constant agitation of the latter: when ebullition has once set in, there is no further need of these precautions. Remove the fluid now from the gas, allow to deposit, pass the clear fluid through a filter, which must not be over-porous, boil the precipitate again with a fresh quantity of solution of soda, then wash it, first by decantation, afterwards on the filter with hot water. Acidify the alkaline filtrate with hydrochloric acid, boil with some chlorate of potassa (to destroy any traces of organic matter), concentrate by evaporation, and precipitate the alumina as directed § 105, *a*.* The boiling of the precipitated oxides with the solution of soda is effected best in a somewhat capacious silver or platinum dish. A solution of soda containing alumina and silica must be particularly avoided.

If sesquioxide of chromium was present in the analyzed substance, you will find the principal portion of it with the sesquioxide of iron; but a small quantity has been oxidized to chromic acid, and is accordingly found in the fluid filtered from the alumina.

b. The method described in *a* is often employed also in a modified form, omitting the reduction of the sesquioxide of iron; in which case the process is performed as follows:—Precipitate with ammonia, decant, filter, wash, transfer the precipitate still moist to a platinum dish, without the aid of water, and remove the last particles adhering to the filter by means of warm hydrochloric acid, which is allowed to drop into the platinum dish. The aqueous washings of the filter are kept separate. When the precipitate in the platinum dish has dissolved, add, very cautiously, concentrated solution of caustic potassa, or carbonate of soda, until the free acid is almost neutralized, and apply heat, finally to boiling; after this, remove the lamp, and add a lump of pure hydrate of potassa sufficiently large to redissolve the precipitated alumina, leaving the hydrated sesquioxide of iron undissolved. Rinse the platinum dish now into the beaker which contains the washings of the filter; wash the sesquioxide of iron, first by decantation, then upon the filter with boiling water, and treat the filtrate as in *a*.

If the fluid in which it is intended to separate sesquioxide of iron and alumina contains lime or magnesia, some alumina is likely to remain undissolved.

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* Journ. f. prakt. Chem. 45, 261.

c. ALUMINA FROM SESQUIOXIDE OF IRON AND PROTOXIDES OF IRON, COBALT, AND NICKEL.

Fuse the oxides with hydrate of potassa in a silver crucible, boil the mass with water, and filter the alkaline fluid, which contains the alumina, from the oxides, which are free from alumina, but contain potassa (H. ROSE). **67**

2. *Different behavior of the Oxides towards Ammonia in the presence of Chloride of Ammonium.*

ALUMINA AND SESQUIOXIDE OF IRON FROM PROTOXIDE OF MANGANESE.

The solution should be sufficiently dilute, mixed with chloride of ammonium, and slightly acid. Heat to boiling, add ammonia in moderate excess, and allow to boil gently without interruption till all free ammonia is expelled, then filter off the precipitate which contains the sesquioxide of iron and the alumina from the fluid containing the manganese. If the quantity of the manganese is small, the precipitate will contain merely unweighable traces of it. If, on the other hand, much is present, the precipitate after being partially washed is redissolved in hydrochloric acid, and the above precipitation is repeated. Results good (H. ROSE*). **68**

3. *Different deportment of neutralized Solutions at boiling heat.*

SESQUIOXIDE OF IRON FROM PROTOXIDES OF MANGANESE, NICKEL AND COBALT, OXIDE OF ZINC, AND OTHER STRONG BASES.

Mix the dilute solution largely with chloride of ammonium (at least 20 of NH_4Cl to 1 of oxide), add carbonate of ammonia in small quantities, at last drop by drop and in very dilute solution, as long as the precipitated iron redissolves, which takes place promptly at first, but more slowly towards the end. As soon as the fluid has lost its transparency, without showing, however, the least trace of a distinct precipitate in it, and fails to recover its clearness after standing some time in the cold, but, on the contrary, becomes rather more turbid than otherwise, the reaction may be considered completed. When this point has been attained, heat slowly to boiling, and keep in ebullition for a short time after the carbonic acid has been entirely expelled. The sesquioxide of iron separates as a basic salt, which rapidly settles, if the solution was not too concentrated. Add now a drop of ammonia, to see whether the iron has been completely thrown down, then a little more ammonia, to convert the basic salt of iron, which has a tendency to dissolve upon cooling, into hydrated sesquioxide, and filter. To insure accurate results, the fluid must not contain more than 3·4 grm. sesquioxide of iron in the litre, and must be tolerably free from sulphuric acid, since it is difficult in presence of the latter to hit the exact point of saturation. (HERSCHEL,† SCHWARZENBERG.‡) The precipitate should be washed with water containing chloride of ammonium. **69**

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* Pogg. Annal. 110, 304 u. 307. † Annal. de Chim. et de Phys. 49, 306.
‡ Annal. d. Chem. u. Pharm. 97, 216.

4. *Method based on the behavior of the Acetates at a boiling heat.*

SESQUIOXIDE OF IRON AND ALUMINA FROM PROTOXIDE OF MANGANESE, OXIDE OF ZINC, PROTOXIDE OF COBALT, AND (but not so well) PROTOXIDE OF NICKEL.

70 Precipitate the sesquioxide of iron and alumina according to § 113, 1, *d*. See also § 81, *e*. The precipitate is free from manganese, cobalt, and zinc; but it contains some nickel, from which it can only be freed by redissolving (after slight washing), reprecipitating in the same manner, and repeating the operation a third time. The method is more suited to the separation of sesquioxide of iron, or of sesquioxide of iron and alumina, than of alumina alone. Results good.

5. *Method based on the different behavior of the Succinates.*

SESQUIOXIDE OF IRON (AND ALUMINA) FROM OXIDE OF ZINC, AND PROTOXIDES OF MANGANESE, NICKEL, AND COBALT.

71 The solution should contain no considerable quantity of sulphuric acid. If acid, as is usually the case, add ammonia till the color is reddish brown, then acetate of soda, or of ammonia (H. ROSE) till the color is deep red, finally precipitate with neutral alkaline succinate at a gentle heat, and filter the succinate of sesquioxide of iron from the solution which contains the rest of the metals. For the further treatment of the precipitate, see § 113, 1, *c*. With proper care the separation is complete, and especially to be recommended when a relatively large quantity of iron is present. The method may also be used in the presence of alumina. The latter falls down completely with the iron. (E. MITSCHERLICH, PAGELS*.)

6. *Different deportment of several Sulphides with Acids, or of the Acetic Acid Solutions with Sulphuretted Hydrogen.*

[*a*. OXIDE OF ZINC FROM PROTOXIDES OF NICKEL AND COBALT. BRUNNER'S METHOD.†

72 The metals must exist in dilute nitric or hydrochloric solution (not more than 1 grm. of both oxides in ½ litre). This is so nearly neutralized by carbonate of soda that only a very small quantity of free acid remains. To accomplish this purpose it is best to add a dilute solution of carbonate until a slight precipitate is left, after agitating and standing for some time, and then to remove this by one or more drops of dilute acid. Conduct into the liquid thus prepared hydrosulphuric acid, which, after a time, produces a perfectly white precipitate of sulphide of zinc. After a good share of the zinc has thus been thrown down, add to the liquid a few drops of a very dilute solution of acetate of soda and continue the passage of hydrosulphuric acid gas as long as the precipitate appears to increase, and afterwards let the whole stand 12 hours at ordinary temperatures. The precipitate settles perfectly and washes easily upon the filter.

In order to make certain of the thorough separation of the zinc, add to a portion of the filtered liquid a drop of solution of acetate of soda and treat again with hydrosulphuric acid gas. If a white turbidity ensues the whole filtrate must be subjected to the same operation.

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* Jahresber. v. Kopp u. Will. 1858, 617.

† Dingler's polyt. Journ. 150, 370.

The sulphide of zinc is further treated according to § 108, 2.

This separation succeeds only when the directions are strictly adhered to. If the solution be neutral, or contain too much acetate of soda, or be heated, nickel will go down with the zinc. If iron be present it must be previously separated. MIXTER has employed this method in the analysis of German silver with most satisfactory results.]

b. PROTOXIDES OF COBALT AND NICKEL FROM PROTOXIDE OF MANGANESE AND THE OXIDES OF IRON.

73 The solution, which must be free from nitric acid, is, after neutralization of any free acid which may be present by ammonia, precipitated with sulphide of ammonium, and highly dilute hydrochloric acid, or—if manganese alone has to be separated—acetic acid then added, and sulphuretted hydrogen gas conducted into the fluid to saturation, with frequent stirring. This serves to dissolve the sulphide of manganese and the sulphide of iron, whilst the sulphide of cobalt and the sulphide of nickel, though the latter less completely, remain undissolved. The filtrate is reprecipitated by addition of ammonia and sulphide of ammonium, and the above treatment is repeated. The results are accurate. It is advisable, however, to test the weighed cobalt and nickel compounds, for manganese and iron.

c. PROTOXIDES OF COBALT AND NICKEL FROM PROTOXIDE OF MANGANESE AND OXIDE OF ZINC.

74 *α.* Put the weighed mixture of the oxides in a porcelain or platinum boat, insert this into a tube, heat to dull redness, whilst conducting sulphuretted hydrogen gas over it. Let the sulphides formed cool in the current of gas, and then digest them for several hours with cold dilute hydrochloric acid, which dissolves only the sulphide of manganese (and sulphide of zinc). The sulphides of nickel and cobalt are left behind pure (EBELMEN[*]).

β. Precipitate with carbonate of soda, filter, wash, and ignite; mix 1 part of the residue with 1·5 of sulphur and 0·75 of carbonate of soda, and heat the mixture in a small retort as strongly as possible for half an hour. Allow the mixture to cool, and extract the sulphide of zinc (and sulphide of manganese) formed, with dilute hydrochloric acid (1 part acid to 10 water), BRUNNER.[†]

7. *Different deportment of the several Oxides with Hydrogen Gas at a red heat.*

SESQUIOXIDE OF IRON FROM ALUMINA AND SESQUIOXIDE OF CHROMIUM.

75 [Precipitate with ammonia, heat, filter, ignite and weigh. Triturate, and weigh off a portion in a platinum crucible. Ignite to redness in a stream of hydrogen gas as long as water forms (about 1 hour). Then ignite over the blast-lamp in a current of mixed hydrogen and hydrochloric acid gases.

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[*] Annal. d. Chem. u. Pharm. 72, 329. Ebelmen has given his method simply for the separation of cobalt and nickel from manganese.

[†] Annal. d. Chem. u. Pharm. 80, 364. Brunner has given his method simply for nickel and zinc.

This leaves the alumina and sesquioxide of chromium in a state of purity; the iron volatilizes as protochloride, and is determined by the loss. (Method of RIVOT and DEVILLE modified.)]

8. *Different capacity of the several Oxides to be converted into higher Oxides, or higher Chlorides.*

a. SESQUIOXIDE OF CHROMIUM FROM ALL THE OXIDES OF THE FOURTH GROUP.

Fuse the oxides with nitrate of potassa and carbonate of soda **76** (comp. § 157), boil the mass with water, add a sufficient quantity of spirit of wine, and heat gently for several hours. Filter, and determine in the filtrate the chromium as directed § 130, and in the residue the bases of the fourth group. The following is the theory of this process: the oxides of zinc, cobalt, nickel, iron, and partly that of manganese, separate upon the fusion, whilst, on the other hand, manganate (perhaps also some ferrate) and chromate of potassa are formed. Upon boiling with water, part of the manganic acid of the manganate of potassa is converted into permanganic acid at the expense of the oxygen of another part, which is reduced to the state of binoxide; the latter separates, whilst the potassa salts are dissolved. The addition of alcohol, with the application of a gentle heat, effects the decomposition of the manganate and permanganate of potassa, binoxide of manganese being separated. Upon filtering the mixture, we have therefore now the whole of the chromium in the filtrate as alkaline chromate, and all the oxides of the fourth group on the filter. Alumina, if present, will be found partly in the residue, partly as alkaline aluminate in the filtrate; proceed with the latter according to **49.**

If you have to deal with the native compound of sesquioxide of chromium with protoxide of iron (chromic iron) the above method does not answer. In this case the following plan may be adopted:

Take 0·5 grm. of the impalpable powder, and fuse in a capacious **77** platinum crucible with 6 grm. bisulphate of potassa for fifteen minutes, at a temperature scarcely above the fusing point of the latter, then raise the heat somewhat, so that the bottom of the crucible may just appear red, and keep it so for fifteen or twenty minutes. The fusing mass should not rise higher than half way up the crucible. The mass begins to fuse quietly, and abundant fumes of sulphuric acid escape. At the expiration of twenty minutes the heat is increased as much as necessary to drive out the second equivalent of sulphuric acid, and even to decompose partially the sulphate of iron and chromium. To the fused mass now add 3 grm. pure carbonate of soda, heat to fusion, and add in small portions from time to time during an hour 3 grm. nitre, maintaining a gentle red heat all the while, then heat for 15 minutes to bright redness. Treat the cold mass with boiling water, filter hot, wash the residue with hot water, then digest in the heat with hydrochloric acid. If anything remains undissolved, it is a portion of the ore undecomposed, and must be subjected again to the above operation. To weigh such a residue and deduct it from the ore first taken is not good, as it never possesses the composition of the original substance. The alkaline solution, which often contains, besides the chromic acid, also some silicic, titanic, and manganic acids and alumina, is evaporated with excess of nitrate of ammonia on a water-bath nearly to dryness, and till all free ammonia is expelled. On addition of water, the silicic acid, alumina, titanic acid, and sesquioxide of manganese remain undissolved, while the chromic acid passes into solution, and is to be determined according to § 130. (T. S. Hunt. F. A. Genth[*].)

b. Protoxide of Manganese from Alumina, Protoxide of Nickel, and Oxide of Zinc (but not from protoxide of cobalt and the oxides of iron).

After Schiel.[†]—Conduct chlorine gas into the solution mixed **78** with acetate of soda (see **59, 60** and **61**).

9. *Method based upon the different deportment of the Nitrites.*

Protoxide of Cobalt from Protoxide of Nickel, also from Protoxide of Manganese and Oxide of Zinc.

The separation of cobalt as nitrite of sesquioxide of cobalt and **79** potassa, which was recommended first by Fischer,[‡] afterwards by A. Stromeyer[‖] is unquestionably the best method for separating cobalt and nickel. The best mode of proceeding is as follows:—The solution of the oxides (from which any iron [as well as all alkaline earths where nickel is present,] must first be separated) is evaporated to a small bulk, and then, if much free acid is present, neutralized with potassa. Then add a concentrated solution of nitrite of potassa (previously neutralized with acetic acid and filtered from any flocks of silica and alumina that may have separated) in sufficient quantity and finally acetic acid, till any flocculent precipitate that may have formed from excess of potassa has redissolved and the fluid is decidedly acid. Allow it to stand at least for 24 hours in a warm place, take out a portion of the supernatant fluid with a pipette, mix it with more nitrite of potassa and observe whether a further precipitation takes place in this after long standing. If no precipitate is formed the whole of the cobalt has fallen down, otherwise the small portion must be returned to the principal solution, some more nitrite of potassa added, and after long standing the same test applied. Thus alone can the analyst be sure of the complete precipitation of the cobalt. Finally filter and treat the precipitate according to § 111, 4, if you desire to determine it after the method of Genth and Gibbs. H. Rose recommends washing the precipitate with a saturated solution of chloride of potassium or of sulphate of potassa, then dissolving it in hydrochloric acid, precipitating the protoxide of cobalt from the solution with potassa, washing, igniting in hydrogen, washing the metal and finally weighing.

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[*] Zeitschrift f. analyt. Chem. 1, 498.

[†] Sillim. Journ. 15, 275. Schiel speaks only of the separation of manganese from iron (?) and nickel; but it is obvious that its separation from alumina and zinc may be effected by the same method.

[‡] Pogg. Annal. 72, 477.

[‖] Annal. d. Chem. u. Pharm. 96, 218.

10. *Method based on the different behavior of the Phosphates.*

MANGANESE FROM NICKEL AND COBALT.

Mix the warm solution of the sulphates or chlorides with chloride of ammonium and ammonia, then with phosphoric acid (the ammonia must remain still in large excess). The white precipitate is $2\,MnO, NH_4O, PO_5 + 2\,HO$ (which on ignition becomes $2\,MnO, PO_5$), the filtrate contains the whole of the nickel. If cobalt is present the precipitate must be dissolved in hydrochloric acid and reprecipitated with ammonia, in order to free it from the small quantity of cobalt which first falls down with it. The precipitate becomes crystalline soon after falling, it is to be washed with solution of chloride of ammonium containing free ammonia (T. H. HENRY[*]). [See also § 109, 3.] **80**

The test-analyses are satisfactory.

11. *Methods based upon the different deportment with Cyanide of Potassium.*

a. ALUMINA FROM OXIDE OF ZINC, PROTOXIDE OF COBALT, AND PROTOXIDE OF NICKEL.

Mix the solution with carbonate of soda, add cyanide of potassium in sufficient quantity, and digest in the cold, until the precipitated carbonates of zinc, cobalt and nickel are redissolved. Filter off the undissolved alumina, wash, and remove the alkali which it contains, by resolution in hydrochloric acid and reprecipitation by ammonia (FRESENIUS and HAIDLEN[†]). **81**

b. PROTOXIDE OF NICKEL FROM PROTOXIDE OF COBALT.

LIEBIG'S Method.[‡]—Mix the solution of the two oxides, which must be free from other oxides, with hydrocyanic acid, then with solution of potassa, and warm, until everything is dissolved. (Cyanide of potassium, free from cyanate, may be used instead of hydrocyanic acid and potassa.) The solution looks reddish-yellow; heat to boiling to remove the free hydrocyanic acid. By this process the double cyanide of cobalt and potassium ($K\,Cy, Co\,Cy$) in the solution is mostly converted, with evolution of hydrogen, into cobalticyanide of potassium ($K_3\,Co_2\,Cy_6$)[‖] whilst the double cyanide of nickel and potassium in the solution remains unaltered. Let the solution cool, then supersaturate with chlorine, and constantly redissolve the precipitate of cyanide of nickel which forms, by addition of solution of soda or potassa. The chlorine does not act upon the cobalticyanide of potassium, but it decomposes the double cyanide of nickel and potassium, and throws down the whole of the nickel as black peroxide. [This must be washed, dissolved, and reprecipitated to separate impurities. It is safest to weigh as metallic nickel.] **82**

To determine the cobalt in the filtrate, supersaturate with acetic acid, boil, precipitate the boiling solution with sulphate of copper, keep in ebullition for some time longer, then filter the fluid from the precipitated cobalticyanide of copper ($Cu_3\,Co_2\,Cy_6 + 7\,HO$); decompose the latter by boiling with solution of potassa, and calculate the quantity of the cobalt from that of the oxide of copper obtained. [Or evaporate to dryness with excess of hydrochloric acid, dissolve the residue in water, separate the cobalt as sulphide, convert into sulphate and oxide, and weigh as metallic cobalt. The best method of separating a little nickel from much cobalt. (GAUHE.*)]

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[*] Phil. Mag. 16, No. 106, 197.

[†] Annal. d. Chem. u. Pharm. 43, 129.

[‡] Ibid. 65, 244, and 87, 128.

[‖] $2\,(Co\,Cy.\,K\,Cy) + K\,Cy + H\,Cy = (K_3\,Co_2\,Cy_6) + H$.

c. PROTOXIDE OF NICKEL FROM OXIDE OF ZINC.

Mix the concentrated solution of both oxides with an excess of concentrated pure solution of potassa, then with solution of hydrocyanic acid in sufficient quantity to redissolve the precipitate completely; add solution of monosulphide of *potassium*, allow the precipitated sulphide of zinc to deposit at a gentle heat, filter, and determine the nickel in the filtrate by heating for some time with fuming hydrochloric acid and nitric acid, or, instead of the latter, chlorate of potassa, evaporating, and finally precipitating with potassa (WÖHLER†). **83**

12. *Volumetric Determination of one of the Oxides.*

a. SESQUIOXIDE OF IRON FROM ALUMINA.

Precipitate both oxides with ammonia (§ 105, *a*, and § 113, 1). **84** Dissolve the weighed residue, or an aliquot part of it, by digestion with concentrated hydrochloric acid, or by fusion with bisulphate of potassa [or better, carbonate of soda], and treatment with water containing sulphuric acid; and determine the iron volumetrically as directed § 113, 3, *a*, or *b*. When hydrochloric acid is used to dissolve the oxides, the solution should be evaporated with excess of sulphuric acid, to remove the hydrochloric acid, in case permanganate is employed for estimating the iron. The alumina is found from the difference. This is an excellent method, and to be recommended more particularly in cases where the relative amount of iron is small. If you have enough substance it is of course much more convenient to divide the solution, by weighing or measuring, into two equal portions, and determine in the one the sesquioxide of iron + alumina, in the other the iron. Instead of estimating the iron by volumetric analysis, you may also precipitate it, after addition of tartaric acid and ammonia, with sulphide of ammonium.

b. SESQUIOXIDE OF IRON FROM PROTOXIDE OF IRON (OXIDE OF ZINC, PROTOXIDE OF NICKEL).

Determine in a portion of the substance the total amount of the **85** iron as sesquioxide, or by the volumetric way. Dissolve another portion by warming with sulphuric acid in a flask through which carbonic acid is conducted, to exclude the air; dilute the solution, and determine the protoxide of iron volumetrically (§ 112, 2, *a*). The difference gives the quantity of the sesquioxide. Or, dissolve the compound in like manner in hydrochloric acid, and determine the sesquichloride of iron with hyposulphite of soda, according to § 113, 3, *b*. In this case the difference gives the protoxide of iron. If it is desired to determine the protochloride of iron in the hydrochloric acid solution with permanganate, the remarks on p. 198 must be borne

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[*] Fres. Zeitschrift, v. 83.

[†] Annal. d. Chem. u. Pharm. 89, 376.

in mind. These convenient and simple methods deserve to replace the older and more complicated methods of determining protoxide of iron in presence of sesquioxide. If the compound in which sesqui- and protoxide of iron are to be estimated is only with difficulty decomposed by acids, heat it with a mixture of 4 parts sulphuric acid and 1 part water in a sealed tube at 210° (Mitscherlich, Jour. f. prakt. Chem., 81, 108, and 83, 455), or, if this is not enough, fuse it with borax (1 part mineral, 5—6 vitrified borax) in a small retort, connected with a flask containing nitrogen (produced by combustion of phosphorus in air); an atmosphere of carbonic acid is less suitable. Triturate the fused mass, and dissolve in boiling hydrochloric acid, in an atmosphere of carbonic acid (Hermann; v. Kobell).

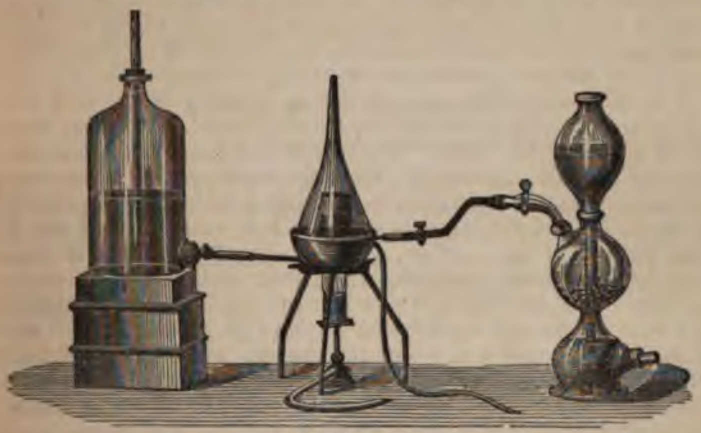

Fig. 67.

[Cooke* dissolves silicates in a mixture of sulphuric and hydrofluoric acids in an atmosphere of steam and carbonic acid, and measures the protoxide of iron by means of permanganate of potassa.

Fig. 67 exhibits his apparatus. To the sides of a copper water-bath are attached three tubes. The tube on the left connects with a Mariotte's flask to maintain the water at a constant level. The upper tube on the right connects with a carbonic acid gas generator, while the third tube carries off any overflow of water to the sink.

On the cover of the water-bath close to the rim is a circular groove, which receives the edge of an inverted glass tunnel. When the apparatus is in use this groove is kept full of water by the spray from the boiling liquid and thus forms a perfect water joint; but in order to secure this result the bath must be kept nearly full of water and holes for the reay escaped of the steam and spray should be provided in the rings, which cover the bath and adapt it for vessels of various sizes. By this arrangement the funnel may be kept filled with an atmosphere of steam or of carbonic acid for an indefinite period. Moreover we can either pour in fresh quantities of solvent, or we can stir up the material, in the vessel within, introducing a tube-funnel or stirrer through the spout of the covering funnel.

[* Am. Jour. Science, 2d ser., xliv., 347.]

The finely pulverized substance (½—1 grm.) is placed in a large platinum crucible. Upon it pour a mixture of dilute sulphuric acid (sp. gr. 1·5) with as little hydrofluoric acid as experience may show is required to dissolve or decompose the substance, stirring up the material with a platinum spatula. The crucible is next transferred to the water-bath, the covering funnel put in place, water poured into the groove, the interior filled with carbonic acid, and the lamp lighted. As soon as the water boils, the supply of carbonic acid is stopped, and if the water level has been properly adjusted, the apparatus will take care of itself, the groove will be kept full of water and the interior of the funnel full of steam. If the materials cake on the bottom of the crucible,—as is not unfrequently the case when a large amount of insoluble sulphate is formed,—the lamp may be removed, the apparatus again filled with carbonic acid, and the contents of the crucible stirred up by aid of a stout platinum wire about two inches long, fused to the end of a glass tube. Anything adhering to the rod can easily be washed back into the crucible by directing the jet from the wash bottle down the throat of the covering funnel. The lamp may then be replaced, the current of carbonic acid interrupted, and the process of digestion continued. When the decomposition is complete the current of carbonic acid gas is re-established, the lamp extinguished, and the air-tube of the Mariotte's flask raised until its lower end is above the level of the overflow. A slow current of water is thus caused to flow through the bath, which soon cools down the whole apparatus. The crucible may now be removed, its contents washed into a beaker glass, and the solution diluted with pure water until the volume is about 500 c. c., when the amount of protoxide of iron present can be determined with a solution of permanganate of potassa in the usual way. The total amount of iron present being subsequently determined, the relative proportion of the two oxides is of course well known.]

Iron may also be determined volumetrically in presence of oxide of zinc, protoxide of nickel, &c. It is, indeed, often the better way, instead of effecting the actual separation of the oxides, to determine in one portion of the solution the sesquioxide of iron + oxide of zinc or + protoxide of nickel, in another portion the iron alone, and to find the quantity of the other metal by the difference. However, this can be done only in cases where the quantity of iron is relatively small.

IV. SEPARATION OF SESQUIOXIDE OF IRON, ALUMINA, PROTOXIDE OF MANGANESE, LIME, MAGNESIA, POTASSA, AND SODA.

§ 161.

As these oxides are found together in the analysis of most silicates, and also in many other cases, I devote a distinct paragraph to the description of the methods which are employed to effect their separation.

1. *Method based upon the employment of Carbonate of Baryta* (particularly applicable in cases where the mixture contains only a small proportion of lime).

Precipitate the iron—which must be present in the form of ses- **86** quioxide—and the alumina by carbonate of baryta,* and, after removing the baryta, separate the two metals, by one of the methods given in § 160. Precipitate the manganese from the filtrate, either by yellow sulphide of ammonium (**55**) or, after addition of a little hydrochloric acid and saturation with chlorine, by carbonate of baryta (**60**). If you have used sulphide of ammonium, which I generally prefer, dissolve the precipitated sulphide of manganese in hydrochloric acid, mix the solution with some sulphuric acid, filter, and determine the manganese as directed § 109, 2 or 3. If you have used carbonate of baryta as precipitant, separate the manganese as directed § 159. Precipitate the dilute solution now with sulphuric acid, filter, and wash the precipitate until the water running off is no longer rendered turbid by chloride of barium; then precipitate the lime after addition of ammonia with oxalate of ammonia. Filter, evaporate the filtrate to dryness, ignite the residue, and separate the magnesia from the alkalies by one of the methods given in § 153.

2. *Application of Alkaline Acetates or Formiates.*

Remove from the solution, by evaporation, any very considerable excess of acid which may be present, then dilute again with water, add carbonate of soda,† until the fluid is nearly neutral (no permanent precipitate must be formed), then acetate or formiate of soda, and proceed as in § 113, 1, *d* (p. 202). Wash the precipitate well, dry, ignite, and weigh. Dissolve in concentrated hydrochloric acid, and determine the iron volumetrically, according to § 113, 3, *b* (p. 203), or fuse with carbonate of soda, dissolve in dilute sulphuric acid, and determine the iron as in § 113, 3, *a* (p. 203). The difference gives the quantity of the alumina. If any silicic acid remains behind on dissolving the precipitate, it is to be collected on a filter, ignited, weighed, and deducted from the alumina. The filtrate contains the manganese, the alkaline earths, and the alkalies. Precipitate the manganese with sulphide of ammonium (**55**) or bromine (**59-61**)—if the former precipitant is employed, boil with hydrochloric acid and filter off the sulphur—precipitate the lime, after addition of ammonia, with oxalate of ammonia, and lastly, after removing the ammonia salts by ignition, precipitate the magnesia from the hydrochloric acid solution of the residue with phosphate of soda. However, if it is intended to estimate the alkalies, the magnesia must be separated by one of the processes in § 153, 4. This method is convenient, and gives good results. **87**

The following methods are particularly suitable in cases where no manganese is present.

3. *Application of Ammonia.*

The solution must contain all the iron in the state of sesquioxide. Add a relatively large quantity of chloride of ammonium, and—observing the precautions indicated in **68**—precipitate with ammonia. **88**

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* Before adding the carbonate of baryta, it is *absolutely indispensable* to ascertain whether a solution of it in hydrochloric acid is completely precipitated by sulphuric acid, so that the filtrate leaves no residue upon evaporation in a platinum dish.

† In cases where it is intended to estimate the alkalies in the filtrate, carbonate and acetate of ammonia must be used instead of the soda salts.

The precipitate contains the whole of the iron and almost the whole of the alumina (a very minute quantity of the latter often remains in solution), also a trace of magnesia. Decant and filter; wash, ignite, and weigh the precipitate, and treat according to one of the methods in § 160. If silicic acid remains undissolved, it is to be determined and deducted. If there is a large excess of alumina or magnesia, mix the hydrochloric acid or sulphuric acid solution with pure potassa in excess, heat, filter, and in the precipitate separate the sesquioxide of iron from any traces of magnesia that may be present according to **58**, *a*. The solution filtered from the alumina and sesquioxide of iron is mixed with hydrochloric acid and concentrated by evaporation, the manganese is precipitated and determined according to § 109, 2, as sulphide, the alkaline earths and alkalies in the filtrate are estimated according to **87**. The weighed sulphide of manganese is digested with hydrochloric acid, any residue that may remain fused with bisulphate of potassa, and the mixed solutions tested according to **66**, to see if they contain alumina.

4. *Decomposition of the Nitrates* (Deville's *method*).

This method presupposes that the bases are combined with nitric acid only. **89**

Proceed first as in **38**. The escape of nitrous acid fumes, observed during the heating of the nitrates, is no proof of the total decomposition of the nitrates of sesquioxide of iron and alumina, as these vapors may owe their formation to the conversion of the nitrate of protoxide of manganese into binoxide. Stop the application of heat when no more vapors are evolved, and the substance has acquired a uniform black color. After the treatment with nitrate of ammonia, the solution contains nitrates of lime, magnesia, and the alkalies, the residue contains alumina, sesquioxide of iron and binoxide of manganese. (That some manganese is dissolved, under certain circumstances, has been stated already in **62**; this trace is found with the magnesia, and finally separated from the latter.)

Deville recommends the following methods to effect the further separation of the bases:—

a. Heat the *residue* with moderately strong nitric acid, until the alumina and sesquioxide of iron are dissolved, leaving the residuary binoxide of manganese of a pure black color. Ignite the residue, and weigh the protosesquioxide of manganese formed. Evaporate the solution in a platinum crucible, ignite, and weigh the mixture of sesquioxide of iron and alumina, which may possibly also contain some protosesquioxide of manganese. Treat a portion of it by the method described in **75**; this gives the alumina. If manganese was present, the iron cannot be estimated by difference. Deville therefore evaporates the solution of the protochlorides (**75**), with sulphuric acid, ignites gently, and treats the residue, which consists of sesquioxide of iron and some sulphate of protoxide of manganese, with water to dissolve the latter. (Should the heat applied have been too strong, which might possibly lead to the decomposition also of sulphate of protoxide of manganese, the residue is moistened with a mixture of oxalic acid and nitric acid, some sulphuric acid added, and the process repeated.)

b. From the *filtrate*, precipitate first the lime by oxalate of ammonia, then separate the magnesia from the alkalies as directed § 153, 4.

This method is particularly suitable in the absence of manganese.

5. *Method which combines* 3 *and* 4.

Precipitate with ammonia (**37**), decant, filter, wash, remove the still half-moist precipitate, as far as practicable, from the filter, dissolve the rest in nitric acid, transfer this to the dish, to effect also the solution of the bulk of the precipitate; proceed as in **89**, and add the fluid, separated from the sesquioxide of iron and alumina, and still containing small quantities of magnesia, to the principal filtrate. This method is often employed with the best success in my laboratory, in absence of manganese; the determination of the alumina being effected by estimating the total amount of sesquioxide of iron and alumina, then the sesquioxide of iron volumetrically (**87**). **90**

Supplement to the Fourth Group.

To §§ 158, 159, 160.

SEPARATION OF SESQUIOXIDE OF URANIUM FROM THE OTHER OXIDES OF GROUPS I.—IV.

It has already been stated, in § 114, that sesquioxide of uranium cannot be completely separated from the *alkalies* by means of ammonia, as the precipitated ammonio-sesquioxide of uranium is likely to contain also fixed alkalies. This precipitate should therefore be dissolved in hydrochloric acid, the solution evaporated in the platinum crucible, the residue gently ignited in a current of hydrogen gas (see fig. 47, p. 181), the chlorides of the alkali metals extracted with water, and the protoxide of uranium ignited in hydrogen, in order to its being weighed as such, or in the air, whereby it is converted into protosesquioxide. Instead of dissolving the precipitate in hydrochloric acid and treating the solution as directed, you may heat the precipitate cautiously* with chloride of ammonium, and treat the residue with water (H. ROSE). **91**

From *baryta*, sesquioxide of uranium may be separated by sulphuric acid, from *strontia* and *lime*, by sulphuric acid and alcohol. Ammonia fails to effect complete separation of sesquioxide of uranium from the alkaline earths, the uranium precipitate always containing not inconsiderable quantities of the earths. In such precipitates, however, the uranium and the alkaline earth may likewise be separated by gentle ignition with chloride of ammonium and treatment of the residue with water.

Uranium may be precipitated from a solution containing *alkalies and alkaline earths* also by sulphide of ammonium. It must here be borne in mind that the solution must contain a sufficiency of chloride of ammonium and free ammonia, that the precipitate must not be filtered off till after long standing (24—48 hours) in the closed flask, and that no alkaline carbonate may be present. The sulphide of ammonium should be colorless, or slightly yellow, and a large excess **92** sulphuretted hydrogen largely in excess, filter before the excess of sulphuretted hydrogen has had time to escape or become decomposed, wash with sulphuretted hydrogen water, dry, roast, redissolve in nitrohydrochloric acid, evaporate nearly to dryness, add water and hydrochloric acid as above, and precipitate again with sulphuretted hydrogen. This second precipitate is free from zinc; it is treated as directed in § 119, 3 (p. 230).

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* Strong ignition would occasion the volatilization of chloride of uranium.

If cadmium is present, a portion of this metal is likely to remain in solution, in presence of the large amount of hydrochloric acid added. It is therefore necessary, in that case, after conducting the sulphuretted hydrogen gas into the fluid, to add saturated sulphuretted hydrogen water until no more sulphide of cadmium precipitates, and then to proceed as for the separation of copper. The separation of cadmium from zinc requires accordingly also a double precipitation with sulphuretted hydrogen, if the quantity of zinc is in any way considerable. However, with proper attention to the instructions here given, the method gives perfectly satisfactory results.

γ. The other metals of the fifth group comport themselves in this respect similarly to cadmium, *i. e.*, they are not completely precipitated by sulphuretted hydrogen in presence of too much free acid in a concentrated solution. Lead requires the least amount of free acid to be retained in solution; then follow in order of succession, cadmium, mercury, bismuth, copper, silver (M. MARTIN*). The separation of these metals from zinc must, therefore, if necessary, be effected by the same process as that of cadmium from zinc (β, the end).

δ. If hydrochloric acid produces no precipitate in the solution, it is preferred as acidifying agent; in the contrary case, sulphuric acid or nitric acid must be used. In the latter case the fluid must be rather largely diluted. ELIOT and STORER† arrived at the same conclusion as ourselves, and showed that the cause of CALVERT's unfavorable results was the too large dilution of his solutions. For to prevent the precipitation of zinc you have not merely to preserve a certain proportion between the zinc and the free acid, but also a certain degree of dilution. Although I agree with the above-named chemists in the opinion that it is possible to produce a condition of the fluid, under which one precipitation will effect complete separation, still it appears to me better, for practical purposes, to precipitate twice, as this is sure to lead to the desired result.

ε. Long experience in the separation of copper from nickel (and cobalt) has led me to the opinion that a double precipitation is unnecessary. If the solution which is to be treated with sulphuretted hydrogen contains enough free hydrochloric acid and not too much water, the copper falls down absolutely free from nickel, while, on the other hand, if the quantity of free acid is not too large, the filtrate will be quite free from copper.

B. *Special Methods.*

SINGLE OXIDES OF THE FIFTH GROUP FROM SINGLE OR MIXED OXIDES OF THE FIRST FOUR GROUPS.

1. SILVER is most simply and completely separated from the OXIDES **96**

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[*] Journ. f. prakt. Chem. 67, 371.

[†] On the Impurities of Commercial Zinc, &c.—Memoirs of the American Academy of Arts and Sciences. New series. Vol. viii.

OF THE FIRST FOUR GROUPS by means of hydrochloric acid. The hydrochloric acid must not be used too largely in excess, and the fluid must be sufficiently dilute; otherwise a portion of the silver will remain in solution. Care must be taken also not to omit the addition of nitric acid, which promotes the separation of the chloride of silver. The latter should, under these circumstances, be collected and washed on a filter (p. 208 β), as washing by decantation would give too large a bulk of fluid.

2. The separation of MERCURY from the METALS OF THE FIRST FOUR GROUPS may be effected also by ignition, which will cause the volatilization of the mercury or the mercurial compound, leaving the non-volatile bodies behind. The method is applicable in many cases to alloys, in others to oxides, chlorides, or sulphides. If the mercury is estimated only from the loss, the operation is conducted in a crucible; otherwise in a bulb-tube, or a wide glass tube with porcelain boat. **97**

The precipitation of mercury as subchloride with phosphorous acid, according to § 118, 2 (p. 224) is also well adapted for its separation from metals of Group IV. If the mercury is already present as suboxide, it may be separated and determined in a simple manner, by precipitation with hydrochloric acid (§ 117, 1).

3. FROM THOSE BASES WHICH FORM SOLUBLE SALTS WITH SULPHURIC ACID, OXIDE OF LEAD may be readily separated by that acid. The results are very satisfactory, if the rules given in § 116, 3, are strictly adhered to. **98**

If you have lead in presence of baryta, both in form of sulphates, digest the precipitate with a solution of ordinary sesquicarbonate of ammonia, without application of heat. This decomposes the lead salt, leaving the baryta salt unaltered. Wash, first with solution of carbonate of ammonia, then with water, and separate finally the carbonate of lead from the sulphate of baryta, by acetic acid or dilute nitric acid (H. ROSE*). The same object may also be attained by suspending the washed insoluble salts in water and digesting with a clear concentrated solution of hyposulphite of soda at 15—20° (not higher). The sulphate of baryta remains undissolved, the sulphate of lead dissolves. Determine the lead in the filtrate (after § 116, 2) as sulphide of lead (J. LÖWE †).

4. OXIDE OF COPPER FROM ALL OXIDES OF THE FIRST FOUR GROUPS.

a. Acidify the solution with sulphuric acid, and precipitate the copper according to § 119, 1, *c*, with *hyposulphite of soda*,‡ as subsulphide, and determine it as such according to § 119, 3. The filtrate contains the other bases. Evaporate, with addition of nitric acid, filter and determine the other oxides in the filtrate.‖ Results good. **99**

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* Journ. f. prakt. Chem. 66, 166. † Ibid. 77, 75.

‡ The commercial salt is often not sufficiently pure; in which case some carbonate of soda must be added to its solution, and the mixture filtered.

‖ As far back as 1842, C. Himly made the first proposal to employ hyposulphite of soda for the precipitation of many metals as sulphides (Annal. d. Chem. u Pharm. 43, 150). The question, after long neglect, was afterwards taken up again by Vohl (Annal. d. Chem. u. Pharm. 96, 237), and Slater (Chem. Gaz. 1855, 369). Flajolot, however, made the first quantitative experiments (Annal. des Mines, 1853, 641; Journ. f. prakt. Chem. 61, 105). The results obtained by him are perfectly satisfactory.

It has been stated in § 119, 1, *c*, that the solution ought to be free from hydrochloric and nitric acids; however, this is not absolutely necessary; only, in presence of hydrochloric or nitric acid, a much larger proportion of the precipitant is required—in presence of the former, because the subchloride of copper formed is decomposed only by a large excess of hyposulphite of soda; in presence of the latter, because the precipitant begins to act upon the copper salt only after the decomposition of the nitric acid.

100 *b.* Precipitate the copper as *subsulphocyanide* according to § 119, 3, *b*; the other metals remain in solution (Rivot). If alkalies were present and it were desired to determine them in the filtrate, sulphocyanide of ammonium must be used instead of the potassium salt usually employed. This method is particularly well adapted for the separation of copper from zinc. The zinc can be precipitated at once from the filtrate by carbonate of soda. The method is also suitable for separating copper from iron (H. Rose*); in this case it is unnecessary that the sesquioxide of iron be completely reduced by the sulphurous acid added; the separation may be effected, even if the solution becomes blood-red on the addition of the precipitant.

5. Oxide of Copper from Oxide of Zinc.

101 Bobierre† employed the following method with satisfactory results in the analysis of many alloys of zinc and copper:—The alloy is put into a small porcelain boat lying in a porcelain tube, and heated to redness for three-quarters of an hour at the most, a rapid stream of hydrogen gas being conducted over it during the process. The zinc volatilizes, the copper remains behind. Lead also (if that metal be present) is not volatilized in this process.

6. Teroxide of Bismuth from the Oxides of the first Four Groups, with the exception of Sesquioxide of Iron.

102 Precipitate the bismuth according to § 120, 4 (p. 234), as basic chloride, and determine it as metal; all the other bases remain completely in solution. Results very satisfactory (H. Rose ‡).

7. Oxide of Cadmium from Oxide of Zinc.

103 Prepare a hydrochloric or nitric acid solution of the two oxides as neutral as possible, add a sufficient quantity of tartaric acid, then solution of potassa or soda, until the reaction of the clear fluid is distinctly alkaline. Dilute now with a sufficient quantity of water, and boil for 1½—2 hours. All the cadmium precipitates as hydrated oxide free from alkali (to be determined as directed § 121), whilst the whole of the zinc remains in solution; the latter metal is determined as directed in § 108, 1, *b* (Aubel and Ramdohr‖). The test-analyses communicated are satisfactory.

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* Pogg. Annal. 110, 424.

† Compt. rend. 36, 224; Journ. f. prakt. Chem. 58, 380,

‡ Pogg. Annal. 110, 429.

‖ Annal d. Chem. u. Pharm. 103, 33.

II. SEPARATION OF THE OXIDES OF THE FIFTH GROUP FROM EACH OTHER.

§ 163.

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“ oxide of mercury, 106, 117.

1. *Methods based upon the Insolubility of certain of the Chlorides.*

a. OXIDE OF SILVER FROM OXIDE OF COPPER, OXIDE OF CADMIUM, TEROXIDE OF BISMUTH, OXIDE OF MERCURY, AND OXIDE OF LEAD.

α. To separate *oxide of silver* from *oxide of copper*, *oxide of cadmium*, and *teroxide of bismuth*, add to the nitric acid solution containing excess of nitric acid, hydrochloric acid as long as a precipitate forms, and separate the precipitated chloride of silver from the solution which contains the other oxides, as directed § 115, 1, *a*. **104**

β. If you wish to separate *oxide of mercury* from *oxide of silver* by hydrochloric acid, special precautions must be taken, as a solution of nitrate of mercury possesses the property of dissolving chloride of silver (WACKENRODER, v. LIEBIG[*]). Although the chloride of silver in solution for the most part separates on the addition of enough hydrochloric acid to convert the nitrate of mercury into chloride, or on addition of acetate of soda, still we cannot depend upon the complete precipitation of the silver. On this account, mix the nitric acid solution—which may not contain any suboxide of mercury, and is to be in a sufficiently dilute condition and acidified with nitric acid—with hydrochloric acid, as long as a precipitate forms. Allow to deposit, filter off the clear fluid, heat the precipitate—to free it from any possibly coprecipitated basic mercury salts—with a little nitric acid, add water, then a few drops of hydrochloric acid, and filter off the chloride of silver. In the filtrate determine the mercury as sulphide (§ 118, 3), and finally test this for silver, by ignition in a stream of hydrogen—any silver that may happen to be present will remain behind in the metallic state.

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[*] Annal. d. Chem. u. Pharm. 81, 128.

γ. In the separation of *silver* from *lead*, the precipitation is also preceded by addition of acetate of soda. The fluid must be hot and the hydrochloric acid rather dilute; no more must be added of the latter than is just necessary. In this manner the separation may be readily effected, since chloride of lead dissolves in acetate of soda (ANTHON). The lead is thrown down from the filtrate by sulphuretted hydrogen.

δ. The volumetric method (§ 115, 5) is usually resorted to in the mint to determine the *silver in alloys*. In presence of oxide of mercury, acetate of soda is mixed with the fluid immediately before the addition of the solution of chloride of sodium.

b. SUBOXIDE OF MERCURY FROM OXIDE OF MERCURY, OXIDE OF COPPER, OXIDE OF CADMIUM, AND OXIDE OF LEAD.

Mix the highly dilute cold solution with hydrochloric acid, as **105** long as a precipitate (subchloride of mercury) forms; allow this to deposit, filter on a weighed filter, dry at 100°, and weigh. The filtrate contains the other oxides. If you have to analyse a solid body, insoluble in water, either treat directly, in the cold, with dilute hydrochloric acid, or dissolve in highly dilute nitric acid, and mix the solution with a large quantity of water before proceeding to precipitate. Care must always be taken that the mode of solution is such as not to endanger the oxidation of the suboxide of mercury. If lead is present the washing of the subchloride must be executed with special care with water of 60—70°, till the filtrate ceases to be colored with sulphuretted hydrogen. As an additional security, it is well to test at last whether the weighed subchloride leaves no sulphide of lead behind on cautious ignition with sulphur in a stream of hydrogen.

c. OXIDE AND SUBOXIDE OF MERCURY FROM OXIDE OF COPPER, OXIDE OF CADMIUM, AND (but less well) FROM OXIDE OF LEAD.

If mercury is present as oxide or as oxide and suboxide, it is **106** precipitated according to § 118, 2, *a*, by means of hydrochloric acid and phosphorous acid as subchloride. The precipitate, particularly when bismuth is present, is first washed with water containing hydrochloric acid, then with pure water, till the washings are no longer colored with sulphuretted hydrogen (H. ROSE*). In the presence of lead, the remarks in **105** must be attended to.

d. CHLORIDE OF LEAD AND CHLORIDE OF SILVER may be separated also by solution of ammonia, which dissolves the latter, leaving the former behind as basic chloride of lead. Bear in mind that the chloride of silver must be recently precipitated, and with exclusion of light. The chloride of silver is thrown down from the ammoniacal solution by nitric acid. It is necessary to test the fluid filtered from the chloride of silver with sulphuretted hydrogen to ascertain whether weighable quantities of chloride of silver may not be retained in solution by the agency of the ammonia salts. **107**

2. *Methods based upon the Insolubility of Sulphate of Lead.*

OXIDE OF LEAD FROM ALL OTHER OXIDES OF THE FIFTH GROUP.

Mix the nitric acid solution with pure sulphuric acid in not too slight excess, evaporate until the sulphuric acid begins to volatilize, allow the fluid to cool, add water (in which, if there is a sufficient quantity of free sulphuric acid present, the sulphates of mercury and of bismuth dissolve completely), and then filter the solution, which contains the other oxides, *without delay*, from the undissolved sulphate of lead. Wash the precipitate with water containing sulphuric acid, displace the latter with spirit of wine, dry, and weigh (§ 116, 3). Precipitate the other oxides from the filtrate by sulphuretted hydrogen. If *oxide of silver* is present in any notable quantity, this method cannot be recommended, as the sulphate of silver is not soluble enough. In this case you may follow ELIOT and STORER,† viz., mix the solution with nitrate of ammonia, warm, precipitate the greater portion of the silver with chloride of ammonium, evaporate the filtrate, remove the ammonia salts by ignition, and in the residue separate the small remainder of the silver from the lead with sulphuric acid as just directed. For the separation of *lead from bismuth*, on the above principle, H. ROSE‡ gives the following process as the best. If both oxides are in dilute nitric acid solution, as is usually the case, evaporate to small bulk, and add enough chloride of ammonium to dissolve all the teroxide of bismuth; the lead separates partially as chloride. Should a portion of the clear fluid poured off become turbid on the addition of a drop of water, you must add some more hydrochloric acid, till no permanent turbidity is produced unless several drops of water are added. The turbid fluids should all be returned, and the glasses rinsed with alcohol. Add now dilute sulphuric acid, allow to stand some time with stirring, add spirit of wine of 0·8 sp. gr., stir well, allow to settle for a long time, filter, wash the sulphate of lead first with alcohol, mixed with a small quantity of hydrochloric acid, then with pure alcohol. Determine it after § 116, 3. Mix the filtrate at once with a large quantity of water, and proceed with the precipitated basic chloride of bismuth according to § 120, 4 (p. 234). **108**

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* Pogg. Annal. 110, 534.

† Proceedings of the American Academy of Arts and Sciences, Sept. 11, 1860, p. 52; Zeitschrift f. Analyt. Chem. 1, 389.

‡ Pogg. Annal. 110, 432.

3. *Different Deportment of the Oxides and Sulphides, with Cyanide of Potassium* (Fresenius and Haidlen [*]).

a. Oxide of Lead and Teroxide of Bismuth from all other Oxides of the Fifth Group.

Mix the *dilute* solution with carbonate of soda in *slight* excess, add solution of cyanide of potassium (free from sulphide of potassium), heat gently for some time, filter, and wash. On the filter you have carbonate of lead and of bismuth, containing alkali; the filtrate contains the other metals as cyanides in combination with cyanide of potassium. The method of effecting their further separation will be learnt from what follows. **109**

b. Oxide of Silver from Oxide of Mercury, Oxide of Copper, and Oxide of Cadmium.

Add to the solution, which, if it contains much free acid, must previously be nearly neutralized with soda, cyanide of potassium until the precipitate which forms at first is redissolved. The solution contains the cyanides of the metals in combination with cyanide of potassium as soluble double salts. Add dilute nitric acid in excess, which effects the decomposition of the double cyanides; the insoluble cyanide of silver precipitates permanently, whilst the cyanide of mercury remains in solution, and the cyanides of copper and cadmium redissolve in the excess of nitric acid. Treat the cyanide of silver as directed § 115, 3, or convert it into the metallic state by ignition in a procelain crucible till the weight remains constant. If the filtrate contains only mercury and cadmium, precipitate at once with sulphuretted hydrogen, which completely throws down the sulphides of the two metals; but if it contains copper, you must first evaporate with sulphuric acid, until the odor of hydrocyanic acid is no longer perceptible, and then precipitate with sulphuretted hydrogen, or with solution of potassa or soda (§ 119, 3 or 1). **110**

c. Oxide of Copper from Oxide of Silver, Oxide of Mercury, and Oxide of Cadmium.

Mix the solution, as in *b*, with cyanide of potassium until the precipitate which is first thrown down redissolves; add some more cyanide of potassium, then sulphuretted hydrogen water or sulphide of ammonium, as long as a precipitate forms. The sulphides of silver, cadmium, and mercury are completely thrown down, whilst the copper remains in solution, as sulphide dissolved in cyanide of potassium. Allow the precipitate to subside, decant repeatedly, treat the precipitate, for security, once more with solution of cyanide of potassium, heat gently, filter, and wash the sulphides of the metals. To determine the copper in the filtrate, evaporate the latter, with addition of nitric and sulphuric acids, until there is no longer any odor of hydrocyanic acid perceptible, and then precipitate with solution of potassa or soda (§ 119, 1), or determine it as subsulphide (§ 119, 3). **111**

d. All the Metals of the Fifth Group from each other.

Mix the dilute solution with carbonate of soda, then with **112** cyanide of potassium in excess, digest some time at a gentle heat, and filter. On the filter you have carbonate of lead and of bismuth, containing alkali; separate the two metals by a suitable method. Add to the filtrate dilute nitric acid in excess, and filter the fluid from the precipitated cyanide of silver, which determine as directed § 115, 3. Neutralize the filtrate with carbonate of soda, add cyanide of potassium, and pass sulphuretted hydrogen in excess. Add now some more cyanide of potassium, to redissolve the sulphide of copper which may have fallen down, and filter the fluid, which contains the whole of the copper, from the precipitated sulphide of mercury and sulphide of cadmium. Determine the copper as directed in *c*, and separate the mercury and cadmium as in **106**.

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[*] Annal. d. Chem. u. Pharm. 43, 129.

4. *Formation and Separation of insoluble Basic Salts.*

Teroxide of Bismuth from Oxide of Copper and Oxide of Cadmium (also from the oxides of the first four groups, with the exception of oxide of iron).

Precipitate the bismuth as basic chloride according to § 120, 4 (p. 234) and throw down the copper and cadmium in the filtrate by sulphuretted hydrogen. Results thoroughly satisfactory (H. Rose[*]). **113**

Teroxide of Bismuth from Oxide of Lead and Oxide of Cadmium.

Separate the bismuth according to § 120, 1, *c*, as basic nitrate, and precipitate the lead and cadmium in the filtrate by sulphuretted hydrogen. Results very satisfactory (J. Löwe[†]). **114**

Teroxide of Bismuth and Oxide of Copper from Oxide of Lead and Oxide of Cadmium.

Separate the bismuth after § 120, 1, *c*, as basic nitrate, then heat the dish on the water-bath till the neutral nitrate of copper is completely converted into bluish-green basic salt and no blue solution is produced on addition of water. Allow to cool, treat with an aqueous solution of nitrate of ammonia (1 in 500), filter, wash with the same solution, and separate in the solution lead from cadmium; in the residue copper from bismuth. Results very satisfactory (J. Löwe, *loc. cit.*).

5. *Precipitation of the Copper as Subsulphocyanide.*

Oxide of Copper from Oxide of Cadmium [and the oxides of Groups I.—IV. (Comp. **100**.)]

Precipitate the copper according to § 119, 3, *b*, as subsulphocyanide (Rivot), and the cadmium from the filtrate as sulphide. Results good (H. Rose). **115**

6. *Different Deportment of the Chromates.*

Bismuth from Cadmium.

Precipitate the bismuth as directed § 120, 2. The filtrate contains the whole of the cadmium. Concentrate by evaporation, and then precipitate the cadmium by the cautious addition of carbonate of soda, as directed § 121, 1, *a* (J. Löwe,[‡] W. Pearson[‖]). The results are said to be satisfactory. **116**

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[*] Pogg. Annal. 110, 430.

[†] Journ. f. prakt. Chem. 74, 345.

[‡] Journ. f. prakt. Chem 67, 469.

[‖] Phil. Mag. xi. 204.

7. *Different Deportment of the Sulphides with Acids.*

a. Oxide of Mercury from Silver, Bismuth, Copper, Cadmium, and (but less well) from Lead.

Boil the thoroughly washed precipitated sulphides with perfectly pure moderately dilute nitric acid. The sulphide of mercury is left undissolved, the other sulphides are dissolved. Absence of chlorine is indispensable. G. v. Rath* employed this method, which is so universally used in qualitative analysis, with perfect success for the separation of mercury from bismuth. **117**

b. Oxide of Copper from Oxide of Cadmium.

Boil the well-washed precipitates of the sulphides with dilute sulphuric acid (1 part concentrated acid and 5 parts water), and, after some time, filter the undissolved sulphide of copper, to be determined according to § 119, 3, from the solution containing the whole of the cadmium (A. W. Hofmann†). **118**

8. *Volatility of some of the Metals, Oxides, Chlorides, or Sulphides.*

a. Mercury from Silver, Lead, Copper (in general from the metals forming non-volatile chlorides). **119**

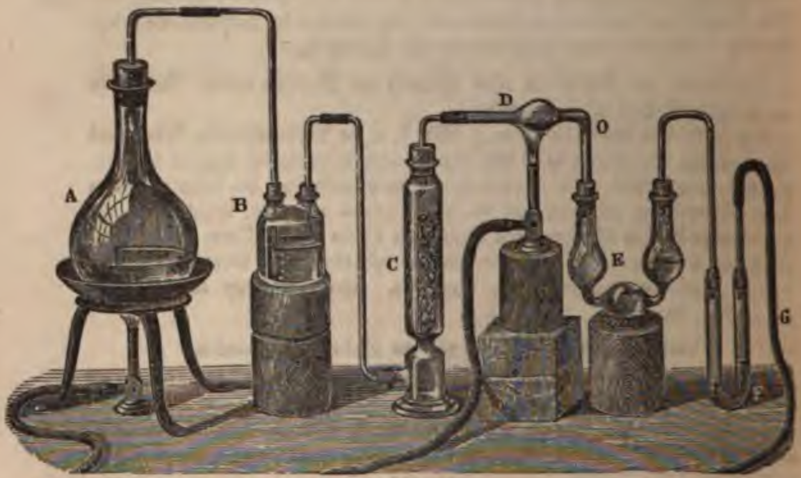

Fig. 68.

Precipitate with sulphuretted hydrogen, collect the precipitated sulphides on a weighed filter, dry at 100°, weigh, and mix uniformly. Introduce an aliquot part into the bulb D (fig. 68), [better into a porcelain tray contained in a plain piece of Bohemian combustion tube bent like D, O,] pass a slow stream of chlorine gas (see p. 324), and apply a gentle heat to the bulb, increasing this gradually to faint redness. Connect G during the operation with a carboy containing moist hydrate of lime. First chloride of sulphur distils over, which decomposes with the water in the tubes *E* and *F* (p. 325); then the chloride of mercury formed volatilizes, condensing partly in the receiver *E*, partly in the hind part of the tube *O*. Cut off that part of the tube, [or withdraw the tray,] rinse the sublimate with water into *E*, and mix the contents of the latter with the water in *F*. Warm the solution until the smell of chlorine has gone off, and then determine in the fluid filtered from the sulphur which may still remain undissolved, the mercury as directed § 118. If the residue consists of chloride of silver alone, or chloride of lead alone, you may weigh it at once; but if it contains several metals, you must reduce the chlorides by ignition in a stream of hydrogen gas, and dissolve the reduced metals in nitric acid, for their ulterior separation. Bear in mind that, in presence of lead, the sulphides and the chlorides must be heated *gently*, in the chlorine and hydrogen respectively, otherwise some chloride of lead might volatilize.

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* Pogg. Annal. 96, 322.

† Annal. d. Chem. u. Pharm. 115, 286.

If it is intended to determine the mercury by the difference, instead of in the direct way, the apparatus may be much simplified. In this case, however, great care must be bestowed on the drying of the sulphides at 100°, because, for instance, the sulphide of lead on drying first becomes lighter from loss of moisture, then gradually heavier again by absorption of oxygen. Hence the method should only be adopted when a small quantity only of another metal is present with the mercury. Weigh the dried precipitate every half hour, and take the lowest weight as the correct one. Then ignite an aliquot part of the precipitate in the stream of hydrogen in a crucible with perforated cover, or in a tube with porcelain tray. The method cannot be applied unless only *one* metal is present with the mercury. From the residue in the crucible or boat reckon how much the whole precipitate, dried at 100°, would have yielded, then calculate the result into sulphide, in which form the substance was contained in the dried precipitate—the difference is sulphide of mercury.

By ignition in hydrogen sulphide of silver yields the metal, sulphide of copper yields the subsulphide, sulphide of lead remains unaltered. Results good.

In alloys or mixtures of oxides the mercury may usually be determined with simplicity from the loss on ignition.

b. TEROXIDE OF BISMUTH FROM OXIDE OF SILVER, OXIDE OF LEAD, AND OXIDE OF COPPER.

The separation is effected exactly in the same way as that of mercury from the same metals (**119**). The method is more especially convenient for the separation of the metals in alloys. Care must be taken not to heat too strongly, as otherwise chloride of lead might volatilize; nor to discontinue the application of heat too soon, as otherwise bismuth would remain in the residue. Put water containing hydrochloric acid in the tubes *E* and *F* (fig. 68), and determine the bismuth therein according to § 120. **120**

9. ***Precipitation of one Metal by another in the Metallic State.***

OXIDE OF LEAD FROM TEROXIDE OF BISMUTH.

Precipitate the solution with carbonate of ammonia, wash the **121** precipitated carbonates, and dissolve in acetic acid, in a flask; place a weighed rod of pure lead upright in the solution and nearly fill up with water, so that the rod may be entirely covered by the fluid; close the flask, and let it stand for about 12 hours, with occasional shaking. Wash the precipitated bismuth off from the lead rod, collect on a filter, wash, and dissolve in nitric acid; evaporate the solution, and determine the bismuth as directed § 120. Determine the lead in the filtrate as directed § 116. Dry the leaden rod, and weigh; subtract the loss of weight which the rod has suffered in the process, from the amount of the lead obtained from the filtrate (ULLGREN).

10. *Separation of Silver by Cupellation.*

CUPELLATION was formerly the universal method of determining **122** SILVER in alloys with COPPER, LEAD, &c. The alloy is fused together with a sufficient quantity of pure lead to give to 1 part of silver 16 to 20 parts of lead, and the fused mass is heated, in a muffle, in a small cupel made of compressed bone-ash. Lead and copper are oxidized, and the oxides absorbed by the cupel, the silver being left behind in a state of purity. One part by weight of the cupel absorbs the oxide of about 2 parts of lead; the quantity of the sample to be used in the experiment may be estimated accordingly. This method is one of the safest processes to determine very small quantities of silver in alloys.* With regard to details, I refer to the "Silver Assay," § 226.

11. *Volumetric Determination of Silver in Presence of Lead and Copper.*

See § 115, 5, II. (p. 215). **123**

12. *Methods based on the behavior of Ammoniacal Solutions of Subchloride of Copper and of Oxide of Silver with each other.*

If you pour a solution of ammonio-subchloride of copper, containing large excess of ammonia, into a solution of nitrate of silver likewise supersaturated with ammonia, a precipitate of metallic silver is immediately formed.

On this reaction MILLON and COMMAILLE† base the following methods of separation:—

a. DETERMINATION OF OXIDE OF SILVER IN PRESENCE OF OXIDE OF LEAD AND OXIDE OF COPPER.

Mix with ammonia in excess, filter, add excess of ammonio-sub- **124** chloride of copper, allow the precipitate to subside, filter it off, wash with ammoniacal water, ignite, and weigh. The test-analyses that have been adduced are perfectly satisfactory. Very small quantities of the precipitated metallic silver I should prefer to dissolve in nitric acid, evaporating to dryness, and determining the silver after PISANI'S method (p. 215).

b. DETERMINATION OF SUBOXIDE OF COPPER IN THE PRESENCE OF THE OXIDE.

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* Compare Malaguti and Durocher, Compt. rend. 29, 689; Dingler, 115, 276.

† Compt. rend. 56, 309; Zeitschrift f. analyt. Chem. 2, 212.

125 Dissolve the compound in hydrochloric acid, add excess of ammonia, then excess of solution of nitrate of silver, which has been mixed with so much ammonia that no separation of chloride of silver can take place. All these operations must be performed in an apparatus through which hydrogen (washed with ammoniacal silver solution) is passing. The precipitated silver is finally determined as in **124**. 1 eq. of the same corresponds to 1 eq. Cu_2O or Cu_2Cl. The total amount of the copper is best determined in another portion of the substance.

SIXTH GROUP.

TEROXIDE OF GOLD—BINOXIDE OF PLATINUM—PROTOXIDE OF TIN—BINOXIDE OF TIN—TEROXIDE OF ANTIMONY—(ANTIMONIC ACID)—ARSENIOUS ACID—ARSENIC ACID.

I. SEPARATION OF THE OXIDES OF THE SIXTH GROUP FROM THE OXIDES OF THE FIRST FIVE GROUPS.

§ 164.

Index :—The Nos. refer to those in the margin.
Gold, from the oxides of Groups I.—III., 126, 131.
" IV., 126, 129, 131.
" silver, 129, 146.
" mercury, 129, 131, 141.
" lead, 129, 150.
" copper, 129, 131.
" bismuth, 129, 131, 150.
" cadmium, 129, 131.
Platinum from the oxides of Groups I.—III., 126.
" " IV., 126, 130, 132.
" silver, 130.
" mercury, 130, 132.
" lead, 130.
" copper, 130, 132.
" bismuth, 130, 132.
" cadmium, 130, 132.
Tin from the oxides of Groups I. and II., 126, 134, 140.
" " III., 126, 134.
" zinc, 126, 128, 133, 134.
" manganese, 126, 128, 134.
" nickel and cobalt, 126, 128, 133, 134, 139.
" iron, 126, 128.
" silver, 127, 128, 133, 139.
" mercury, 127, 128, 133.
" lead, 127, 128, 133, 139.
" copper, 127, 128, 133, 134, 139.
" bismuth, 127, 128.
" cadmium, 127, 128, 133.
Antimony from the oxides of Groups I. and II., 126, 140.
" " III., 126.
" zinc, 126, 128.
" manganese, 126, 128.
" nickel and cobalt, 126, 128, 138, 139.
" iron, 126, 128, 137.
" silver, 127, 128, 139.
" mercury, 127, 128, 135, 147.
" lead, 127, 128, 139, 149.
" copper, 127, 128, 137.
" bismuth, 127, 128.
" cadmium, 127, 128.

Arsenic from oxides of Group I., 126, 140, 144, 145.
" " II., 126, 136, 140, 144, 145, 148.
" " III., 126, 143, 144.
" zinc, 126, 128, 136, 142, 144, 145.
" manganese, 126, 128, 136, 142, 143, 144, 145.
" nickel and cobalt, 126, 128, 136, 138, 139, 142, 143. 144, 145.
" iron, 126, 128, 136, 137, 142, 143, 144.
" silver, 127, 128, 136, 139, 144.
" mercury, 127, 128, 136, 144, 147.
" lead, 127, 128, 136, 139, 142, 144, 148.
" copper, 127, 128, 136, 137, 139, 142, 143, 144.
" bismuth, 127, 128, 136, 144.
" cadmium, 127, 128, 136, 143, 144.

A. *General Methods.*

1. *Method based upon the Precipitation of the Oxides of the Sixth Group from Acid Solutions by Sulphuretted Hydrogen.*

ALL OXIDES OF THE SIXTH GROUP FROM THOSE OF THE FIRST FOUR GROUPS.

126 Conduct into the acid * solution sulphuretted hydrogen in excess, and filter off the precipitated sulphides (corresponding to the oxides of the sixth group).

The points mentioned **95**, α, β, and γ must also be attended to here. As regards γ, antimony and tin are to be inserted between cadmium and mercury, in the order of metals there given. With respect to the particular conditions required to secure the proper precipitation of certain metals of the sixth group, I refer to Section IV. I have to remark in addition:—

α. That sulphuretted hydrogen fails to separate arsenic acid from oxide of zinc, as, even in presence of a large excess of acid, the whole or at least a portion of the zinc precipitates with the arsenic as $\mathrm{Zn\,S, As\,S_5}$ (WÖHLER). To secure the separation of the two bodies in a solution, the arsenic acid must first be converted into arsenious acid, by heating with sulphurous acid, before the sulphuretted hydrogen is conducted into the fluid.

β. That in presence of antimony, tartaric acid should be added, as otherwise the sulphide of antimony will contain chloride.

2. *Method based upon the Solubility of the Sulphides of Metals of the Sixth Group in Sulphides of the Alkali Metals.*

127 *a.* THE OXIDES OF GROUP VI. (with the exception of Gold and Platinum) FROM THOSE OF GROUP V.

Precipitate the acid solution with sulphuretted hydrogen, paying due attention to the directions given in Section IV. under the heads of the several metals, and also to the remarks in **126**. The precipitate consists of the sulphides of the metals of Groups V. and VI. Wash, treat immediately after with yellow sulphide of ammonium in excess, and digest the mixture for some time at a gentle heat; filter off the clear fluid, treat the residue again with sulphide of ammonium, digest a short time, repeat the same operation, if necessary, a third and fourth time, filter, and wash the residuary sulphides of Group V. with water containing sulphide of ammonium. If protosulphide of tin is present, some flowers of sulphur must be added to the sulphide of ammonium, unless the latter be very yellow. In presence of copper, the sulphide of which is a little soluble in [merely warm] sulphide of ammonium, [boil a short time or] use sulphide of sodium instead. However, this substitution can be made only in the absence of mercury, since the sulphides of that metal are soluble in sulphide of sodium.

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* Hydrochloric acid answers best as acidifying agent.

Add to the alkaline filtrate, gradually, hydrochloric acid in small portions, until the acid predominates; allow to subside, and then filter off the sulphides of the metals of the sixth group, which are mixed with sulphur.

SCHNEIDER* states that he failed in effecting complete separation of bisulphide of bismuth from bisulphide of tin by digestion with sulphide of potassium, but succeeded in accomplishing that object by conducting sulphuretted hydrogen into the potassa solution of tartrate of teroxide of bismuth and protoxide of tin (which decompose into binoxide of bismuth and binoxide of tin).

If a solution contains much arsenic acid in presence of small quantities of copper, bismuth, &c., it is convenient to precipitate these metals (together with a very small amount of sulphide of arsenic) by a brief treatment with sulphuretted hydrogen. Filter, extract the precipitate with sulphide of ammonium (or sulphide of potassium), acidify the solution obtained, mix it with the former filtrate containing the principal quantity of the arsenic, and proceed to treat further with sulphuretted hydrogen.

b. THE OXIDES OF GROUP VI. (with the exception of Gold and Platinum) FROM THOSE OF GROUPS IV. AND V. **128**

α. Neutralize the solution with ammonia, add chloride of ammonium, if necessary, and then yellow sulphide of ammonium in excess; digest in a closed flask, for some time at a moderate heat, and then proceed as in **127**. Repeated digestion with fresh quantities of sulphide of ammonium is indispensable. On the filter, you have the sulphides of the metals of Groups IV. and V. Wash with water containing sulphide of ammonium.

In presence of nickel, this method offers peculiar difficulties; traces of sulphide of mercury, too, are liable to pass into the filtrate. In presence of copper (and absence of mercury), soda and sulphide of sodium are substituted for ammonia and sulphide of ammonium.†

β. In the analysis of solid compounds (oxides or salts), it is in most cases preferable to fuse the substance with 3 parts of dry carbonate of soda and 3 of sulphur, in a covered porcelain crucible, over a lamp. When the contents are completely fused, and the excess of sulphur is volatilized, the mass is allowed to cool, and then treated with water, which dissolves the sulphosalts of the metals of the sixth group, leaving the sulphides of Groups IV. and V. undissolved. By this means, even ignited binoxide of tin may be readily tested for iron, &c., and the amount of the admixture determined (H. Rose). The solution of the sulphosalts is treated as in **127**. In the presence of copper, traces of the sulphide may be dissolved with the sulphides of Group VI. Occasionally a little sulphide of iron dissolves, coloring the solution green. In that case add some chloride of ammonium, and digest till the solution has turned yellow.

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* Annal. d. Chem. u. Pharm. 101, 64.

† The accuracy of this method has been called in question by Bloxam (Quart. Jour. Chem. Soc. 5, 119). That chemist found that sulphide of ammonium fails to separate small quantities of bisulphide of tin from large quantities of sulphide of mercury or sulphide of cadmium (1 : 100); and that more especially the separation of copper from tin and antimony (also from arsenic) by this method is a failure, as nearly the whole of the tin remains with the copper. The latter statement I cannot confirm, for Mr. Lucius, in my laboratory, has succeeded in separating copper from tin by means of yellowish sulphide of sodium completely; but it is indispensable to digest three or four times with sufficiently large quantities of the solvent, as stated in the text.

B. *Special Methods.*

1. *Insolubility of some Metals of the Sixth Group in Acids.*

a. Gold from Metals of Groups IV. and V. in Alloys.

α. Boil the alloy with pure nitric acid (not too concentrated), or, **129** according to circumstances, with hydrochloric acid. The other metals dissolve, the gold is left. The alloy must be reduced to filings, or rolled out into a thin sheet. If the alloy were treated with concentrated nitric acid, and at a temperature below boiling, a little gold might dissolve in consequence of the co-operation of nitrous acid. In the presence of silver and lead, this method is only applicable when they amount to more than 80 per cent., since otherwise they are not completely dissolved. Alloys of silver and gold containing less than 80 per cent. of silver are therefore fused together with 3 parts of lead, before they are treated with nitric acid. The residuary gold is weighed; but its purity must be ascertained, by dissolving in cold dilute nitrohydrochloric acid, not in concentrated hot acid, as chloride of silver also is soluble in the latter.

At the Mint Conference held at Vienna in 1857, the following process was agreed upon for the mints in the several states of Germany. Add to 1 part of gold, supposed to be present, 2½ parts of pure silver; wrap both the alloy and the silver in paper together, and introduce into a cupel in which the requisite amount of lead is just fusing.* After the removal of the lead (by absorption), the button of gold and silver is flattened, by hammering or rolling, then ignited, and rolled; the rolls are treated first with nitric acid of 1·2 sp. gr., afterwards with nitric acid of 1·3 sp. gr., rinsed, ignited, and weighed.†

β. Heat the alloy (previously filed or rolled) in a capacious platinum dish with a mixture of 2 parts pure concentrated sulphuric acid and 1 part water, until the evolution of gas has ceased, and the sulphuric acid begins to volatilize; or fuse the alloy with bisulphate of potassa (H. Rose). Separate the gold from the sulphates of the other metals, by treating the mass first with cold, finally with boiling water. It is advisable to repeat the operation with the separated gold, and ultimately test the purity of the latter.

γ. The methods given in *α* and *β* may be united, *i.e.*, the cupelled and thinly-rolled metal may be first warmed with nitric acid of 1·2 sp. gr., then thoroughly washed, the gold boiled 5 minutes with concentrated sulphuric acid, washed again, and ignited (Mascazzini, Bugatti).

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* If the weighed sample, say 0·25 grm., contains 98–92$^0/_0$ gold, 3 grm. of lead are required; if 92–87·5, 4 grm.; if 87·5–75, 5 grm.; if 75–60, 6 grm.; if 60–35, 7 grm.; if less than 35, 8 grm.

† Kunst- und Gewerbeblatt f. Baiern, 1857. 151; Chem. Centralbl. 1857, 307; Polyt Centralbl. 1857, 1151, 1471, 1639.

b. Platinum from Metals of Groups IV. and V., in Alloys.

130 The separation is effected by treating with sulphuric acid, or, better still, with bisulphate of potassa (**129**, *β*); but not with nitric acid, as platinum in alloys will, under certain circumstances, dissolve in that acid.

2. *Separation of Gold in the metallic state.*

Gold from all Oxides of Groups I.—V., with the exception of Oxide of Lead and Oxide of Silver.

131 Precipitate the hydrochloric acid solution with oxalic acid as directed § 123, *b*, *γ*, or with sulphate of iron, § 123, *b*, *α*, and filter off the gold when it has completely separated. Take care to add a sufficient quantity of hydrochloric acid to prevent oxalates insoluble in water precipitating along with the gold, for want of a solvent.

3. *Precipitation of Platinum as Potassio- or Ammonio-bichloride of Platinum.*

Platinum from the Oxides of Groups IV. and V., with the exception of Lead and Silver.

132 Precipitate the platinum with chloride of potassium or chloride of ammonium as directed § 124, and wash the precipitate thoroughly with spirit of wine. The platinum prepared from the precipitated ammonium or potassium salt is to be tested after being weighed, to see whether it yields any metal (especially iron) to fusing bisulphate of potassa.

4. *Separation of Oxides insoluble in Nitric Acid.*

a. Tin from Metals of Groups IV. and V. (not from Bismuth, Iron, or Manganese*) in Alloys.

133 Treat the finely divided alloy, or the metallic powder obtained by reducing the oxides in a stream of hydrogen with nitric acid, as directed § 126, 1, *a*. The filtrate contains the other metals as nitrates. As binoxide of tin is liable to retain traces of copper and lead, you must, in an accurate analysis, test an aliquot part of it for these bodies, and determine their amount as directed **118**, *β*.

Brunner recommends the following course of proceeding, by which the presence of copper in the tin may be effectually guarded against. Dissolve the alloy in a mixture of 1 part of nitric acid, 4 parts of hydrochloric acid, and 5 parts of water; dilute the solution largely with water, and heat gently. Add crystals of carbonate of soda until a distinct precipitate has formed, and boil. (In presence of copper, the precipitate must, in this operation, change from its original bluish-green to a brown or black tint.) When the fluid has been in ebullition some 10 or 15 minutes, allow it to cool, and then add nitric acid, drop by drop, until the reaction is distinctly acid; digest the precipitate for several hours, when it should have acquired a pure white color. The binoxide of tin thus obtained is free from copper; but it may contain some iron, which can be removed as directed in **128**, β.

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* If the alloy of tin contains bismuth or manganese, there remains with the binoxide of tin always teroxide of bismuth or sesquioxide of manganese, which cannot be extracted by nitric acid; if it contains iron, on the contrary, some binoxide of tin always dissolves with the iron, and cannot be separated even by repeated evaporation (H. Rose, Pogg. Annal. cxii. 169, 170, 172).

Before the binoxide of tin can be considered pure, it must be tested also for silicic acid, as it frequently retains traces of this substance. To this end, an aliquot part is fused with 3—4 parts of carbonate of soda and potassa, the fused mass boiled with water, and the solution filtered; hydrochloric acid is then added to the filtrate, and, should silicic acid separate, the fluid is filtered off from this substance. The tin is then precipitated by sulphuretted hydrogen, and the silicic acid still remaining in the filtrate is determined in the usual way (§ 140). If hydrochloric acid has produced a precipitate of silicic acid, the last filtration is effected on the same filter (KHITTEL*).

b. ANTIMONY FROM THE METALS OF GROUPS IV. AND V. IN ALLOYS.

Proceed as in *a*, filter off the precipitate, and convert it by ignition into antimoniate of teroxide of antimony (§ 125, 2). Results only approximative, as a little teroxide of antimony dissolves. Alloys of antimony and lead, containing the former metal in excess, should be previously fused with a weighed quantity of pure lead (VARRENTRAPP†). [See Tookey, Journ. Chem. Soc. xv. 464.]

5. *Precipitation of Binoxide of Tin by Neutral Salts* (e. g., *Sulphate of Soda*) *or by Sulphuric Acid.*

TIN FROM THE OXIDES OF GROUPS I., II., III.; ALSO FROM PROTOXIDE OF MANGANESE, OXIDE OF ZINC, PROTOXIDES OF NICKEL AND COBALT, OXIDE OF COPPER (TEROXIDE OF GOLD).

Precipitate the hydrochloric acid solution, which must contain **134** the tin entirely as binoxide (bichloride), according to § 126, 1, *b*, by nitrate of ammonia or sulphate of soda (LÖWENTHAL), or by sulphuric acid, which, H. ROSE says, answers equally well. Alloys are treated as follows:—First, oxidize by digestion with nitric acid; when no more action takes place, evaporate the greater portion of the nitric acid in a porcelain dish, moisten the mass with strong hydrochloric acid, and after half an hour add water, in which the metachloride of tin and the other chlorides dissolve. Alloys of tin and gold are dissolved in aqua regia, the excess of acid evaporated, and the solution diluted with much water, before precipitating with sulphuric acid.

It must be remembered that in this process any phosphoric acid that may be present is precipitated entirely or partially with the binoxide of tin. After the precipitate has been well washed by decantation, LÖWENTHAL recommends to boil with a mixture of 1 part nitric acid (sp. gr. 1·2) and 9 parts water, then to transfer to the filter, and wash thoroughly. Results very satisfactory. If the fluid contains sesquioxide of iron, a portion of the latter always falls down with the tin. Hence the binoxide of tin must be tested for iron according to **128**, β, and if present, its amount must be determined and deducted.

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* Chem. Centralbl. 1857, 929.

† Dingler's polyt. Journ. 158, 316.

6. *Insolubility of Sulphide of Mercury in Hydrochloric Acid.*

MERCURY FROM ANTIMONY.

Digest the precipitated sulphides with moderately strong hydrochloric acid in a distilling apparatus. The sulphide of antimony dissolves, while the sulphide of mercury remains behind. Expel all the hydrosulphuric acid, then add tartaric acid, dilute, filter, mix the filtrate with the distillate which contains a little antimony, and precipitate with sulphuretted hydrogen. The sulphide of mercury may be weighed as such (F. FIELD*). **135**

7. *Conversion of Arsenic and Antimony into Alkaline Arseniate and Antimoniate.*

a. ARSENIC FROM THE METALS AND OXIDES OF GROUPS II., IV., AND V.

If you have to do with arsenites or arseniates, fuse with 3 parts of carbonate of soda and potassa and 1 part of nitrate of potassa; if an alloy has to be analyzed it is fused with 3 parts of carbonate of soda and 3 parts of nitrate of potassa. In either case the residue is boiled with water, and the solution, which contains the arseniates of the alkalies, filtered from the undissolved oxides or carbonates. The arsenic acid is determined in the filtrate as directed § 127, 2. If the quantity of arsenic is only small, the fusion may be effected in a platinum crucible; but if more considerable, the process must be conducted in a porcelain crucible, as platinum would be injuriously affected by it. In the latter case, bear in mind that the fused mass is contaminated with silicic acid and alumina. If the alloy contains much arsenic a small quantity may be readily lost by volatilization, even though the operation be cautiously conducted. In such a case, therefore, it is better first to oxidize with nitric acid, then to evaporate, and to fuse the residue as above directed with carbonate of soda and nitrate of potassa. **136**

b. ARSENIC AND ANTIMONY FROM COPPER AND IRON, especially in ores containing sulphur.

Diffuse the very finely pulverized mineral through pure solution of potassa, and conduct chlorine into the fluid (comp. p. 327, *A*, *b*). The iron and copper separate as oxides, the solution contains sulphate, arseniate, and antimoniate of potassa (RIVOT, BEUDANT, and DAGUIN†). **137**

c. ARSENIC AND ANTIMONY FROM COBALT AND NICKEL.

Dilute the nitric acid solution with water, add a large excess of potassa, heat gently, and conduct chlorine into the fluid until the precipitate is black. The solution contains the whole of the arsenic and antimony, the precipitate the nickel and cobalt, in form of sesquioxide (RIVOT, BEUDANT, and DAGUIN, *loc. cit.*) **138**

8. *Volatility of certain Chlorides or Metals.*

a. TIN, ANTIMONY, ARSENIC FROM COPPER, SILVER, LEAD, COBALT, NICKEL.

Treat the sulphides with a stream of chlorine, proceeding exactly **139** as directed in **119**. In presence of antimony, fill the tubes E and F (fig. 68) with a solution of tartaric acid in water, mixed with hydrochloric acid. The metals may be also separated by this method in alloys. The alloy must be very finely divided. Arsenical alloys are only very slowly decomposed in this way. If tin and copper are separated in this manner, according to the experience of H. ROSE,* a small trace of tin remains with the chloride of copper. [See TOOKEY, Journ. Chem. Soc. xv., 466.]

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* Quart. Journ. Chem. Soc. 12, 32.

† Compt. rend. 1853, 835; Journ. f. prakt. Chem. 61, 133.

b. BINOXIDE OF TIN, TEROXIDE OF ANTIMONY (AND ALSO ANTIMONIC ACID), ARSENIOUS, AND ARSENIC ACIDS, FROM ALKALIES AND ALKALINE EARTHS.

Mix the solid compound with 5 parts of pure chloride of ammonium in powder, in a porcelain crucible, cover this with a concave platinum lid, on which some chloride of ammonium is sprinkled, and ignite gently until all chloride of ammonium is driven off; mix the contents of the crucible with a fresh portion of that salt, and repeat the operation until the weight remains constant. In this process, the chlorides of tin, antimony, and arsenic, escape, leaving the chlorides of the alkaline and alkaline earthy metals. The decomposition proceeds most rapidly with alkaline salts. With regard to alkaline earthy salts it is to be observed that those which contain antimonic acid or binoxide of tin are generally decomposed completely by a double ignition with chloride of ammonium (magnesia alone cannot be separated perfectly from antimonic acid by this method). The alkaline earthy arseniates are the most troublesome; the baryta, strontia, and lime salts usually require to be subjected 5 times to the operation, before they are free from arsenic, and the arseniate of magnesia it is impossible thoroughly to decompose in this way (H. ROSE†). **140**

c. MERCURY FROM GOLD (SILVER, AND GENERALLY FROM THE NON-VOLATILE METALS).

Heat the weighed alloy in a porcelain crucible, ignite till the weight is constant, and determine the mercury from the loss. If it is desired to estimate it directly, the apparatus, fig. 50, p. 222, may be used. In cases where the separation of mercury from metals that oxidize on ignition in the air is to be effected by this method, the operation must be conducted in an atmosphere of hydrogen (p. 181, fig. 47). **141**

9. *Volatility of Sulphide of Arsenic.*

ARSENIC ACID FROM THE OXIDES OF MANGANESE, IRON, ZINC, LEAD, COPPER, NICKEL, COBALT (NOT OF SILVER, ALUMINUM, OR MAGNESIUM).

Mix the arsenic acid compound (no matter whether it has been air-dried or gently ignited) with sulphur, and ignite under a good draught in an atmosphere of hydrogen (p. 181, fig. 47; the perforated lid must in this case be of porcelain). The whole of the arsenic volatilizes, the sulphides of maganese, iron, zinc, lead, and copper remain behind; they may be weighed directly. After weighing, add a fresh quantity of sulphur to the residue, ignite as before, **142**

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[*] Pogg. Annal. 112, 169.

[†] Ibid. 73, 582; 74, 578; 112, 173.

and weigh again; repeat this operation until the weight remains constant. Usually, if the compound was intimately mixed with the sulphur, the conversion of the arseniate into sulphide is complete after the first ignition. Results very good.

In separating *nickel* the analyst will remember that the residue cannot be weighed directly, since it does not possess a constant composition; hence the ignition in hydrogen may be saved; arseniate of nickel loses all its arsenic on being simply mixed with sulphur and heated. The heat should be moderate and continued, till no more red sulphide of arsenic is visible on the inside of the porcelain crucible. It is advisable to repeat the operation. The separation of arsenic from *cobalt* cannot be completely effected in this manner even by repeated treatment with sulphur, but it can be effected by oxidizing the residue with nitric acid, evaporating to dryness, mixing with sulphur, and re-igniting. Smaltine and cobaltine must be treated in the same manner (H. ROSE[*]). I should not forget to mention that EBELMEN,[†] a long while ago, noticed the separation of arsenic acid from sesquioxide of iron by ignition in a stream of sulphuretted hydrogen.

10. *Separation of Arsenic as Arseniate of Magnesia and Ammonia.*

ARSENIC ACID FROM OXIDE OF COPPER, OXIDE OF CADMIUM, SESQUIOXIDE OF IRON, PROTOXIDE OF MANGANESE, PROTOXIDE OF NICKEL, PROTOXIDE OF COBALT, ALUMINA.

Mix the hydrochloric acid solution, which must contain the whole **143** of the arsenic in the form of arsenic acid, with enough tartaric acid to prevent precipitation by ammonia, precipitate the arsenic acid according to § 127, 2, as arseniate of magnesia and ammonia, allow to settle, filter, wash once with a mixture of 3 parts water and 1 part ammonia, redissolve in hydrochloric acid, add a very minute quantity of tartaric acid, supersaturate again with ammonia, allow to deposit, and determine the now pure precipitate according to § 127, 2. In the filtrate the bases of Groups IV. and V. may be precipitated by sulphide of ammonium; if alumina is present, evaporate the solution filtered from the sulphides with addition of carbonate of soda and a little nitre to dryness, fuse, and estimate the alumina in the residue. The method is more adapted to the separation of rather large than of very small quantities of arsenic from the above named oxides, since in the case of small quantities the minute portions of arseniate of magnesia and ammonia that remain in solution may exercise a considerable influence on the accuracy of the result. [See Editor's note to § 135 e, α.]

11. *Separation of Arsenic as Arseniomolybdate of Ammonia.*

ARSENIC ACID FROM ALL OXIDES OF GROUPS I.—V.

Separate the arsenic acid as directed in § 127, 2, *b*; long continued **144** heating at 100° is indispensable. The determination of the bases is most conveniently effected in a special portion (comp. § 135, k.)

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[*] Zeitschrift f. anal. Chem. 1, 413.

[†] Anal. de Chim. et de Phys. (3) xxv. 98.

12. *Insolubility of Arseniate of Sesquioxide of Iron.*

ARSENIC ACID FROM THE BASES OF GROUPS I. AND II., AND FROM OXIDE OF ZINC, AND THE PROTOXIDES OF MANGANESE, NICKEL, AND COBALT.

Precipitate the arsenic acid, according to circumstances, as directed § 127, 3, *a* or *b*, filter, and determine the bases in the filtrate. **145**

13. *Methods based upon the Insolubility of some Chlorides.*

a. SILVER FROM GOLD.

Treat the alloy with cold dilute nitrohydrochloric acid, dilute, and filter the solution of the terchloride of gold from the undissolved chloride of silver. This method is applicable only if the alloy contains less than 15 per cent. of silver; for if it contains a larger proportion, the chloride of silver which forms protects the undecomposed part from the action of the acid. In the same way silver may be separated also from *platinum*. **146**

b. OXIDE OF MERCURY FROM THE OXYGEN COMPOUNDS OF ARSENIC AND ANTIMONY.

Precipitate the mercury from the hydrochloric solution by means of phosphorous acid as subchloride (§ 118, 2, *a*). The tartaric acid, which in the presence of antimony must be added, does not interfere with the reaction (H. ROSE*). **147**

14. *Insolubility of certain Sulphates in Water or Spirit of Wine.*

a. ARSENIC ACID FROM BARYTA, STRONTIA, LIME, AND OXIDE OF LEAD.

Proceed as for the separation of phosphoric acid from the same oxides (§ 135, *b*). The compounds of these bases with arsenious acid are first converted into arseniates, before the sulphuric acid is added; this conversion is effected by heating the hydrochloric acid solution with chlorate of potassa. **148**

b. ANTIMONY FROM LEAD.

Treat the alloy with a mixture of nitric and tartaric acids. The solution of both metals takes place rapidly and with ease. Precipitate the greater part of the lead as sulphate (§ 116, 3), filter, precipitate with sulphuretted hydrogen, and treat the sulphides according to **128** with sulphide of ammonium, in order to separate the antimony from the lead left unprecipitated by the sulphuric acid (A. STRENG†). **149**

15. *Different deportment with Cyanide of Potassium.*

GOLD FROM LEAD AND BISMUTH.

These metals may be separated in solution by cyanide of potassium in the same way in which the separation of mercury from lead and bismuth is effected (see **109**). The solution of the double cyanide of gold and potassium is decomposed by boiling with aqua regia, and, after expulsion of the hydrocyanic acid, the gold determined by one of the methods given in § 123. **150**

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[*] Pogg. Annal. 110, 536.

[†] Ding. polyt. Journ. 151, 389.

II. SEPARATION OF THE OXIDES OF THE SIXTH GROUP FROM EACH OTHER.

§ 165.

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" tin, antimony, and arsenic, 152.
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" tin, 152, 161.
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" gold, 134, 152, 161,
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1. *Precipitation of Platinum as Potassiobichloride of Platinum.*

PLATINUM FROM GOLD.

Precipitate from the solution of the chlorides the platinum as directed § 124, *b*, and determine the gold in the filtrate as directed § 123, *b*. **151**

2. *Volatility of the Chlorides of the inferior Metals.*

PLATINUM AND GOLD FROM TIN, ANTIMONY, AND ARSENIC.

Heat the finely divided alloy or the sulphides in a stream of chlorine gas. Gold and platinum are left, the chlorides of the other metals volatilize (compare **50**). **152**

3. *Volatility of Arsenic and Tersulphide of Arsenic.*

a. ARSENIC FROM TIN (H. ROSE).

Convert into sulphides or into oxides, dry at 100°, and heat a weighed portion with addition of a little sulphur in a bulb-tube or tray, gently at first, but gradually more strongly, conducting a stream of dry sulphuretted hydrogen gas through the tube during the operation. Sulphur and tersulphide of arsenic volatilize, sulphide of tin is left. The tersulphide of arsenic is received in U-tubes containing dilute ammonia, which are connected with the bulb-tube, in the manner described in **119**. When upon continued application of heat no sign of further sublimation is observed in the colder part of the bulb-tube, drive off the sublimate which has collected in the bulb, allow the tube to cool, and then cut it off above the coating. Divide the separated portion of the tube into pieces, and heat these with a little solution of soda until the sublimate is dissolved; unite the solution with the ammoniacal fluid in the receiver, add hydrochloric acid, then, without filtering, chlorate of **153** potassa, and heat gently until the tersulphide of arsenic is completely dissolved. Filter from the sulphur, and determine the arsenic as directed § 127, 2. The quantity of tin cannot be calculated at once from the blackish-brown sulphide of tin in the bulb, since this contains more sulphur than corresponds to the formula $Sn\,S$. It is therefore weighed, and the tin determined in a weighed portion of it, by converting it into binoxide, which is effected by moistening with nitric acid, and roasting (§ 126, 1, *c*).

Tin and arsenic in alloys are more conveniently converted into oxides by cautious treatment with nitric acid. If, however, it is wished to convert them into sulphides, this may readily be effected by heating 1 part of the finely divided alloy with 5 parts of carbonate of soda, and 5 parts of sulphur, in a covered porcelain crucible, until the mass is in a state of calm fusion. It is then dissolved in water, the solution filtered from the sulphide of iron, &c., which may possibly have formed, and the filtrate precipitated with hydrochloric acid.

If the tin only in the alloy is to be estimated directly, while the arsenic is to be found from the difference, convert as above directed into sulphides or oxides, mix with sulphur and ignite in a porcelain crucible with perforated cover in a stream of sulphuretted hydrogen. The residual arsenic-free protosulphide of tin is to be converted into binoxide and weighed as such.

4. *Methods based upon the insolubility of Antimoniate of Soda.*

a. ANTIMONY FROM TIN AND ARSENIC (H. ROSE).

If the substance is metallic, oxidize the finely divided weighed **154** sample, in a porcelain crucible, with nitric acid of 1·4 sp. gr., adding the acid gradually. Dry the mass on the water-bath, transfer to a silver crucible, rinsing the last particles adhering to the porcelain into the silver crucible with solution of soda, dry again, add eight times the bulk of the mass of solid hydrate of soda, and fuse for some time. Allow the mass to cool, and then treat with hot water until the undissolved residue presents the appearance of a fine powder; dilute with some water, and add one third the volume of alcohol of 0·83 sp. gr. Allow the mixture to stand for 24 hours, with frequent stirring; then filter, transfer the last adhering particles from the crucible to the filter by rinsing with dilute spirit of wine (1 vol. alcohol to 3 vol. water), and wash the undissolved residue on the filter, first with spirit of wine containing 1 vol. alcohol to 2 vol. water, then with a mixture of equal volumes of alcohol and water, and finally with a mixture of 3 vol. alcohol and 1 vol. water. Add to each of the alcoholic fluids used for washing a few drops of solution of carbonate of soda. Continue the washing until the color of a portion of the fluid running off remains unaltered upon being acidified with hydrochloric acid and mixed with sulphuretted hydrogen water.

Rinse the antimoniate of soda from the filter, wash the latter with a mixture of hydrochloric and tartaric acids, dissolve the antimoniate in this mixture, precipitate with sulphuretted hydrogen, and determine the antimony as directed § 125, 1.

To the filtrate, which contains the tin and arsenic, add hydrochloric acid, which produces a precipitate of arseniate of binoxide of tin; conduct now into the unfiltered fluid sulphuretted hydrogen for some time, allow the mixture to stand at rest until the odor of that gas has almost completely gone off, and separate the weighed sulphides of the metals which contain free sulphur, as in **153.**

If the substance contains only *antimony* and *arsenic*, the alcoholic filtrate is heated, with repeated addition of water, until it scarcely retains the odor of alcohol; hydrochloric acid is then added, and the arsenic acid determined as arseniate of magnesia and ammonia (§ 127, 2).

b. Small quantities of the sulphides of arsenic and antimony mixed with sulphur are often obtained in mineral analysis. The two metals may in this case be conveniently separated as follows: Oxidize the precipitate with chlorine-free red fuming nitric acid, evaporate the solution nearly to dryness; mix the residue with a copious excess of carbonate of soda, add some nitrate of soda, and treat the fused mass as given in *a.* If, on the other hand, you have a mixture of sulphides of tin and antimony to analyze, oxidize it with nitric acid of 1·5 sp. gr., and treat the residue obtained on evaporation as given in *a.*

5. *Precipitation of Arsenic as Arseniate of Ammonia-Magnesia.*

a. ARSENIC FROM ANTIMONY.

Oxidize the metals or sulphides with nitrohydrochloric acid or **155** hydrochloric acid and chlorate of potassa, or with chlorine in alkaline solution (p. **327**, *A*, *b*); add tartaric acid, a large quantity of chloride of ammonium, and then ammonia in excess. (Should the addition of the latter reagent produce a precipitate, this is a proof that an insufficient quantity of chloride of ammonium or of tartaric acid has been used, which error must be corrected before proceeding with the analysis.) Then precipitate the arsenic acid as directed § 127, 2, and determine the antimony in the filtrate as directed in § 125, 1. As basic tartrate of magnesia might precipitate with the arseniate of magnesia and ammonia, the precipitate should always, after slight washing, be redissolved in hydrochloric acid, and the solution reprecipitated with ammonia.—An excellent method.

b. ARSENIOUS ACID FROM ARSENIC ACID.

Mix the sufficiently dilute solution with a large quantity of chlo- **156** ride of ammonium, precipitate the arsenic acid as directed § 127, 2, and determine the arsenious acid in the filtrate by precipitation with sulphuretted hydrogen (§ 127, 4). LUDWIG* has observed that if the solution is too concentrated, arsenite of magnesia falls down with the arseniate of magnesia and ammonia, hence it is necessary to dissolve the weighed magnesia precipitate in hydrochloric acid and test the solution with sulphuretted hydrogen. The presence of arsenious acid will be betrayed by the immediate formation of a precipitate.

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* Archiv für Pharm. 97, 24.

c. BINOXIDE OF TIN FROM ARSENIC ACID (LENSSEN[*]).

The oxides obtained by oxidation with nitric acid are digested 157
with ammonia and yellow sulphide of ammonium, and the arsenic precipitated from the clear solution according to § 127, 2, as arseniate of magnesia and ammonia. On acidifying the filtrate the tin separates as bisulphide.

6. *Behavior of the Sulphides towards Bisulphite of Potassa.*

ARSENIC FROM ANTIMONY AND TIN (BUNSEN[†]).

If freshly precipitated sulphide of arsenic is digested with sul- 158
phurous acid and sulphite of potassa, the precipitate is dissolved; on boiling, the fluid becomes turbid from separated sulphur, which turbidity for the most part disappears again on long boiling. The fluid contains, after expulsion of the sulphurous acid, arsenite and hyposulphite of potassa.

$$[2\,\mathrm{As\,S_3} + 8\,(\mathrm{K\,O, 2\,S\,O_2}) = 2\,(\mathrm{KO, As\,O_3}) + 6(\mathrm{K\,O, S_2O_2}) + \mathrm{S_3} + 7\,\mathrm{S\,O_2}]$$

The sulphides of antimony and tin do not exhibit this reaction. Both therefore may be separated from sulphide of arsenic by precipitating the solution of the three sulphides in sulphide of potassium with a large excess of aqueous sulphurous acid, digesting the whole for some time in a water-bath, and then boiling till two-thirds of the water and the whole of the sulphurous acid are expelled. The residuary sulphide of antimony or tin is arsenic-free, the filtrate contains the whole of the arsenic and may be immediately precipitated with sulphuretted hydrogen. BUNSEN determines the arsenic by oxidizing the dried sulphide together with the filter with *fuming* nitric acid, diluting the solution a little, warming *gently* with a little chlorate of potassa (in order to oxidize more fully the substances formed from the paper), and finally precipitating as arseniate of magnesia and ammonia.

With regard to the separation of sulphide of tin from the solution of arsenite of potassa it is to be observed, that the sulphide of tin must be washed with concentrated solution of chloride of sodium, as, if water were used, the fluid would run through turbid. As soon as the precipitate is thoroughly washed with the chloride of sodium solution, the latter is displaced by solution of acetate of ammonia, containing a slight excess of acetic acid. These last washings must not be added to the first, as the acetate of ammonia hinders the complete precipitation of the arsenious acid by sulphuretted hydrogen.

The test-analyses adduced by BUNSEN show very satisfactory results.

7. *Methods based upon the Separation of the Metals themselves, or on the different Deportment of the same with Acids.*

a. TIN FROM ANTIMONY [TOOKEY,[†] CLASSEN[‖]].

[The alloy or mixture must contain 8—10 times as much tin as 159
antimony. If need be, add a weighed amount of pure tin, to establish this proportion.

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[*] Annal. d. Chem. u. Pharm. 114, 116.

[†] Ibid. 106, 3.

[‡] Journ. Chem. Soc. xv. 462.

[‖] Journ. f. prakt. Chem. xcii. 477.

The metals are dissolved in hydrochloric acid and a little nitric acid, the solution is heated nearly to boiling, and then piano wire (soluble without residue in acids) added little by little as long as any iron dissolves. It is necessary that no excess of metallic iron remain. Therefore, when all the antimony appears to be thrown down and all the iron dissolved, add a little hydrochloric acid, and after the precipitate has settled, pour off the clear liquid and observe whether iron will produce any further precipitation. It is thus easy to be certain that all the antimony is separated, and that it is unmixed with metallic iron. Wash the antimony with hot water to which at first *a few drops* of hydrochloric acid are added. Finally, displace the water that adheres to the precipitate by means of absolute alcohol, and the latter by a few drops of ether, and dry at 100°. The tin is separated from the filtrate by sulphuretted hydrogen.]

b. MUCH TIN FROM LITTLE ANTIMONY AND ARSENIC.

If an alloy of the three metals is treated in a very finely divided **160** condition in a stream of carbonic acid with strong hydrochloric acid, the whole of the tin dissolves to protochloride. A part of the arsenic and antimony escapes as arsenetted and antimonetted hydrogen, whilst the rest remains behind in the state of metal, or, as the case may be, of a solid combination with hydrogen. Conduct the gas through several U-tubes, containing a little chlorine-free red fuming nitric acid, whereby the arsenic and antimony will be oxidized. When the solution is effected, dilute the contents of the flask with air-free water to a certain volume, mix, allow to settle and determine the tin in an aliquot part, either gravimetrically or volumetrically. Filter the rest of the fluid, wash the precipitate thoroughly, dry the filter with its contents in a porcelain crucible, add the contents of the U-tubes, evaporate to dryness, and in the residue separate the antimony and arsenic as directed **154**.

c. TIN FROM GOLD.

Gold may be separated from excess of tin by boiling the finely **161** divided alloy with only slightly diluted sulphuric acid, to which hydrochloric acid has been cautiously added. The tin dissolves as protochloride. Heat is applied till the sulphuric acid begins to volatilize copiously. Binoxide of tin is formed which dissolves in the concentrated sulphuric acid, while the gold remains behind. On addition of much water, the binoxide of tin falls, mixed with finely divided gold, in the form of a purple-red precipitate. On warming with concentrated sulphuric acid the binoxide of tin finally redissolves while the gold is left pure (H. ROSE*).

d. PLATINUM FROM GOLD.

The aqua regia solution is freed as far as possible from nitric acid **162** by evaporation with hydrochloric acid, and treated with a solution of protochloride of iron, the gold being determined as directed § 123, *b*. The platinum may be precipitated from the filtrate by sulphuretted hydrogen according to § 124, *c*.

8. *Precipitation of Tin as Arseniate of the Binoxide.*

TIN FROM ARSENIC.

E. HÄFFELY† has proposed the following method of determining both the tin and the arsenic in commercial stannate of soda, which often contains a large admixture of arseniate of soda. Mix a weighed sample with a known quantity of arseniate of soda in excess, add nitric acid also in excess, boil, filter off the precipitate, which has the composition $2\ SnO_2, AsO_5 + 10\ aq.$, and wash; expel the water by ignition, and weigh the residue, which consists of $2\ SnO_2, AsO_5$. In the filtrate determine the excess of arsenic acid as directed § 127, 2. The amount of the binoxide of tin is found from the weight of the precipitate, that of the arsenic acid is obtained by adding the quantity in the precipitate to the quantity in the filtrate, and deducting the quantity added. **163**

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* Pogg. Annal. 112, 172.

† Phil. Mag. x. 220.

9. *Volumetric Methods.*

a. Arsenious from Arsenic Acid.

164 Convert the whole of the arsenic in a portion of the substance into arsenic acid and determine the total amount of this as directed § 127, 5, *b*; determine in another portion the arsenious acid as directed in § 127, 5, *a*, and calculate the arsenic acid from the difference.

b. Teroxide of Antimony from Antimonic Acid.

165 Determine in a sample of the substance the total amount of the antimony as directed § 125, 1, in another portion that of the teroxide as directed § 125, 3, and calculate the antimonic acid from the difference.

c. Protoxide of Tin in Presence of Binoxide.

166 In one portion of the substance convert the whole of the protoxide into binoxide by digestion with chlorine water or some other means, and determine the total quantity of tin as directed § 126, 1, *b*; in another portion, which, if necessary, is to be dissolved in hydrochloric acid in a stream of carbonic acid, determine the protoxide according to § 126, 2.

II. SEPARATION OF THE ACIDS FROM EACH OTHER.

It must not be forgotten that the following methods of separation proceed generally upon the assumption that the acids exist either in the free state, or in combination with alkaline bases; compare the introductory remarks, p. 337. Where several acids are to be determined in one and the same substance, we very often use a separate portion for each. The methods here given do not embrace every imaginable case, but only the most important cases, and those of most frequent occurrence.

FIRST GROUP.

ARSENIOUS ACID—ARSENIC ACID—CHROMIC ACID—SULPHURIC ACID—PHOSPHORIC ACID—BORACIC ACID—OXALIC ACID—HYDROFLUORIC ACID—SILICIC ACID—CARBONIC ACID.

§ 166.

1. Arsenious Acid and Arsenic Acid from all other Acids.

167 Precipitate the arsenic from the solution by means of sulphuretted hydrogen (§ 127, 4, *a* or *b*), filter, and determine the other acids in the filtrate. It must be remembered, that the tersulphide of arsenic will be obtained mixed with sulphur if chromic acid, sesquioxide of iron, or any other substances which decompose sulphuretted hydrogen are present.

From those acids which form soluble salts with magnesia, arsenic acid may be separated also by precipitation as arseniate of magnesia and ammonia as directed § 127, 2.

2. SULPHURIC ACID FROM ALL THE OTHER ACIDS.

*a. From Arsenious, Arsenic, Phosphoric, Boracic, Hydrofluoric, Oxalic, Silicic, and Carbonic Acids.**

Acidify the dilute solution strongly with hydrochloric acid, mix **168** with chloride of barium, and filter the sulphate of baryta from the solution, which contains all the other acids. Determine the sulphate of baryta as directed § 132.

If acids are present with which baryta forms salts insoluble in water but soluble in acids, the sulphate of baryta is apt to carry down with it such salts, and this is all the more liable to happen, the longer the precipitate is allowed to settle. This remark applies especially to the oxalate and tartrate of baryta and the baryta salts of other organic acids (H. ROSE). In such cases I would recommend, after washing, to stop up the neck of the funnel, and digest the precipitate with a solution of bicarbonate of soda, then to wash with water, with dilute hydrochloric acid, and again with water. In every case, however, the purity of the weighed sulphate of baryta must be tested as directed § 132, 1.

b. From Hydrofluoric Acid in Insoluble Compounds.

A mixture of sulphate of baryta and fluoride of calcium cannot **169** be decomposed by simple treatment with hydrochloric acid; the insoluble residue contains, besides sulphate of baryta, sulphate of lime and fluoride of barium. The object in view may be attained, however, by the following process:—Fuse the substance with 6 parts of carbonate of soda and potassa, and 2 parts of silicic acid; allow the mass to cool, treat with water, and add carbonate of ammonia to the solution obtained; filter, wash the separated silicic acid with dilute solution of carbonate of ammonia, supersaturate the filtrate with hydrochloric acid, and precipitate with chloride of barium.

If you wish to determine the fluoride also, acidify with nitric acid, precipitate with nitrate of baryta, then saturate with carbonate of soda, and precipitate the fluoride of barium by spirit of wine. Wash a long time, first with spirit of wine of 50 per cent., then with strong alcohol; dry, ignite, and weigh. The insoluble residue left upon treating with water contains the baryta and lime. Dissolve in hydrochloric acid, separate the silicic acid, and determine the bases as directed § 154 (H. ROSE).

c. In presence of a large proportion of Chromic Acid.

Reduce the chromic acid by boiling the dry compound with con- **170** centrated hydrochloric acid (if this process is conducted after p. 258, it gives, at the same time, the quantity of the chromic acid); dilute the solution largely, and precipitate, first the sulphuric acid by adding chloride of barium in slight excess, then the excess of baryta by sulphuric acid, and lastly the sesquioxide of chromium by ammonia.

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* With respect to the separation of sulphuric acid from selenic acid, comp. Wohlwill (Annal. d. Chem. u. Pharm. 114, 183).

d. From Hydrofluosilicic Acid.

171 Precipitate the hydrofluosilicic acid as directed § 133, then the sulphuric acid in the filtrate by baryta.

3. Phosphoric Acid from the other Acids.

172 *a.* From the *acids of arsenic*, see **167**; from *sulphuric acid*, see **168.**

b. From Chromic Acid.

Precipitate the phosphoric acid as phosphate of magnesia and ammonia (134, *b*). Determine the chromic acid in the filtrate as directed § 130, *a*, β, *b*, *c*, or *d*.

c. From Boracic Acid.

173 Precipitate the phosphoric acid with a solution of chloride of magnesium and chloride of ammonium, and determine it as pyrophosphate of magnesia (§ 134, *b*). Determine the boracic acid in the filtrate as directed § 136, I., *c*.

d. From Oxalic Acid.

174 α. If the two acids are to be determined in one portion, the aqueous solution is mixed with sodio-terchloride of gold in excess, heat applied, and the quantity of oxalic acid present calculated from that of the reduced gold (§ 137, *c*, α). The gold added in excess is separated from the filtrate by means of sulphuretted hydrogen, and the phosphoric acid then precipitated by sulphate of magnesia. If the compound is insoluble in water, hydrochloric acid is used as solvent, and the process conducted as directed § 137, *c*, β.

175 β. If there is enough of the substance, the oxalic acid is determined in one portion according to the direction of § 137, *b* or *d*, and the phosphoric acid in another portion. If the substance is soluble in water, and the quantity of oxalic acid inconsiderable, the phosphoric acid may be precipitated at once with sulphate of magnesia, chloride of ammonium, and ammonia; if not, the substance is ignited with carbonate of soda and potassa, which destroys the oxalic acid, and the phosphoric acid is determined in the residue.

e. Phosphates from Fluorides.

α. *The substance is soluble in water.*

176 *aa.* If the substance contains a *relatively large* quantity of fluorine, which will permit the estimation of the latter from the difference, precipitate the solution with exclusion of air by chloride of calcium with addition of lime-water to alkaline reaction, allow to deposit, decant through a filter, wash the precipitate, dry, ignite, and weigh. It consists of phosphate of lime and fluoride of calcium. Heat an aliquot part in a platinum vessel, with sulphuric acid, until all the fluorine has escaped as hydrofluoric acid, taking care not to raise the heat to a degree at which sulphuric acid volatilizes; then determine the lime and the phosphoric acid as directed § 135, *b*. By deducting the phosphoric acid and lime from the total weight of the precipitate, the fluorine is found by the following proportion:—

The eq. of fluorine less the eq. of oxygen : the eq. of fluorine
: :
the difference found : the fluorine sought.

The fluorine may be determined directly in another aliquot part, by fusing it with acid pyrophosphate of soda, and calculating the fluorine by comparing the actual loss of weight with that which the pyrophosphate would have suffered if ignited alone. $2\,(NaO, HO, PO_5) + Ca\,Fl = NaO, PO_5 + NaO, CaO, PO_5 + H\,Fl + HO$.

[*bb.* If the substance contains a *relatively small* proportion of **177** fluorine, this should be determined directly by Fresenius' method. (**182.**) Phosphoric acid may be estimated in a portion that has been evaporated with sulphuric acid, by molybdic solution (p. 271).]

β. *The substance is not soluble in water, but decomposable by acids* (*e.g.*, apatite, bone-ash).

Dissolve in hydrochloric acid, evaporate with sulphuric acid, as in **178** **176**, until the fluorine is completely expelled, and determine in the residue the phosphoric acid on the one hand, the oxides on the other hand. Now, if you know the proportion between the phosphoric acid and the bases in the analyzed compound, you may readily calculate the expelled fluorine from the excess of the bases, the oxygen of the latter being equivalent to the fluorine. Of course, it is taken for granted that other acids are absent, or are determined in separate portions.

γ. *The substance is insoluble in water and not decomposable by acids.*

Fuse with carbonate of soda and silicic acid as in **169**, treat the **179** fused mass with water, and the solution with carbonate of ammonia. You have now in solution the whole of the fluorine and phosphoric acid in combination with alkali (H. Rose), and may accordingly proceed as in **176** or **177**.

4. Fluorides from Borates.

Mix the solution containing the acids in combination with alkali **180** with some carbonate of soda, and add acetate of lime in excess. A precipitate is formed, which contains the whole of the fluorine as fluoride of calcium, and besides this, carbonate and some borate of lime; the greater proportion of the latter having been redissolved by the excess of the lime salt added. Determine the fluoride of calcium in the precipitate as directed in § 138, I. The small quantity of boracic acid in the precipitate is, in this process, partly volatilized, partly dissolved, after evaporating the mass with acetic acid and extracting with water. It is therefore necessary to determine the boracic acid in a separate portion of the substance; this is effected according to the directions of § 136, 2 (A. Stromeyer[*]).

5. Fluorides from Silicic Acid and Silicates.

A great many native silicates contain fluorides: care must, therefore, always be taken, in the analysis of minerals, not to overlook the latter.

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[*] Annal. d. Chem. u. Pharm. 100, 91.

If the silicates containing fluoride are decomposable by acids—(which is only rarely the case)—and the silicic acid is separated in the usual way by evaporation, the whole of the fluorine may volatilize.

a. BERZELIUS's method.

Fuse the elutriated substance with 4 parts of carbonate of soda, for some time, at a strong red heat; digest the mass in water, boil, filter, and wash, first with boiling water, then with solution of carbonate of ammonia. The filtrate contains all the fluorine as fluoride of sodium, and, besides this, carbonate, silicate, and aluminate of soda. Mix the filtrate with carbonate of ammonia, and heat the mixture, replacing the carbonate of ammonia which evaporates. Filter off the precipitate of hydrate of silicic acid and hydrate of alumina, and wash with carbonate of ammonia. Heat the filtrate until the carbonate of ammonia is completely expelled, and determine the fluorine as directed § 138. To separate the silicic acid, decompose the two precipitates with hydrochloric acid as directed § 140, II., *a.** 181

b. WÖHLER's method modified by FRESENIUS. (Suitable for the analysis of all silicates and phosphates which are readily decomposed by sulphuric acid; those undecomposable by this acid must be fluxed.) 182

[The substance must be reduced to an impalpable powder; if not a silicate, mixed intimately with 10 to 15 times its weight of finely pulverized quartz, and decomposed in a flask with *pure* concentrated sulphuric acid (sp. gr. 1·848), at a temperature not higher than 160° nor lower than 150° C. The fluorine is estimated by collecting and weighing the fluoride of silicon thus evolved (FRESENIUS), or by loss (WÖHLER.) The former is the only accurate method, especially when small quantities are to be determined. To displace fluoride of silicon completely from the mixture evolving it, long-continued aspiration of air is necessary. The apparatus needful consists of a gasholder of 20—30 litres capacity, which should be filled with pure air from out-of-doors; of 3 flasks of about 250 c. c. capacity each; and of 8 light U-tubes, whose bore is 12 mm. and whose legs are 10—12 cm. long. Air is forced from the gasholder,—firstly, through a flask half filled with strong pure sulphuric acid, then through a U-tube containing soda lime, and again through a U-tube filled with glass splinters moistened with strong sulphuric acid. The air thus freed from water and carbonic acid is conducted to the bottom of a second flask, containing the substance under examination drenched with a large excess of sulphuric acid. This flask stands over a lamp upon a plate of cast-iron, and to judge of the temperature of its contents another flask similarly filled with sulphuric acid, in which a thermometer is suspended by a loosely fitting cork, is placed upon the same iron plate, the lamp-flame being stationed between them and equidistant from both. The dry air streaming through the decomposing flask, heated to 150°—160° carries on fluoride of silicon and a little vapor of sulphuric acid, firstly into an empty U-tube, and then into another containing, in the first half, fused (anhydrous) chloride of calcium, and in the second half, pumice, impregnated with anhydrous sulphate of copper (p. 289). The pure fluoride of silicon is finally absorbed in the three remaining U-tubes, and is estimated by their increase of weight. Of these tubes, the first contains, in the leg next the decomposing flask, pumice moistened with water between two cotton plugs; in the bend and half of the other leg, soda lime; lastly, fused chloride of calcium between cotton plugs. The weight of this tube should be 40–50 grm. To complete the absorption, the next (seventh) U-tube is filled half with fused soda-lime and half with fused chloride of calcium; and the last (eighth) contains glass splinters wet with pure and strong sulphuric acid, to completely retain traces of water, which would otherwise be carried off by the large volume of heated air.

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* The whole of the silicic acid may be removed from the filtrate by the treatment with carbonate of ammonia: addition of carbonate of zinc and ammonia, as recommended by Berzelius, and afterwards by Regnault, appears therefore superfluous (H. Rose).

The tubes having been carefully adjusted, and made tight by melting sealing-wax over the corks, so much substance is placed in the decomposing flask as to yield, if possible, 0·1 grm. of fluoride of silicon. If a carbonate be present, this must be removed by heating the weighed substance with water and a slight excess of acetic acid (in case of operating with a fluoride soluble in water, acetate of lime must also be added). After the carbonate is decomposed, the whole is evaporated to dryness on the water-bath. The residue is digested and washed with water, dried, separated as well as possible from the filter, and mixed with the filter-ash. The substance is intimately mixed, if needful, with ignited quartz powder transferred to the decomposing flask, the mortar being rinsed with quartz-powder, and drenched with 40—50 c. c. of concentrated sulphuric acid. The flask is connected with the tubes on either side, and with frequent shaking is gradually brought to a temperature of 150°—160° C. Incipient decomposition is recognized by the rise of gas bubbles in the heated liquid (which are broken by agitation) as well as by deposition of silica in the tube containing moist pumice. As soon as gas-bubbles cease to appear, which commonly happens after an hour, when small quantities (0·1 grm.) of a fluoride are employed, or after two to three hours when larger amounts (1.0 grm.) are used, the lamp is removed, the air current stopped, and the three weighed absorption tubes are weighed again. During this operation the break in the system of tubes is supplied by a straight glass tube. After weighing, the three tubes are replaced, the decomposing flask is heated again to 150°–160° C,, the air-current is re-established, and the experiment continued $\frac{1}{2}$–$1\frac{1}{2}$ hours. If the tubes suffer no further increase of weight, the operation is concluded; otherwise the heating, &c., must be repeated until a constant weight is obtained.

For every hour during which the air-current has been passing the apparatus, deduct 0·001 grm. from the total increase of the three absorption tubes; the residue is fluoride of silicon. This multiplied by $\frac{Fl_2}{Si\,Fl_2}=\frac{38}{52}=0{\cdot}73077$, gives the fluorine. Results good.]

6. FLUORIDES, SILICATES, AND PHOSPHATES, IN PRESENCE OF EACH OTHER.

Native compounds of fluorides, silicates, and phosphates are not **183** uncommon. They are decomposed as in **181**. Complete decomposition of the phosphates is not always effected in this process, as phosphate of lime, for instance, is only partially decomposed by fusion with carbonate of soda. The solution remaining after the removal of the silicic acid and the volatilization of the carbonate of ammonia, contains—in presence of phosphates—besides fluoride of sodium and carbonate of soda, also phosphate of soda.

184 Neutralize the fluid nearly with hydrochloric acid, precipitate with chloride of calcium, filter, dry, and ignite the precipitate, which consists of fluoride of calcium, phosphate of lime, and carbonate of lime; treat the residue with acetic acid in excess, and evaporate on the water-bath to dryness and complete expulsion of the acetic acid; extract the acetate of lime, into which the carbonate has been converted by the last operation, with water; weigh the residue, which consists of phosphate of lime and fluoride of calcium; and treat it further as directed in **176**. In the original residue of the first operation and in the precipitate thrown down by carbonate of ammonia, determine the silicic acid, the rest of the phosphoric acid, and the bases. The method **182** may also be employed for estimating fluorine.

7. Silicic Acid from all other Acids.

a. In Compounds which are decomposed by Hydrochloric Acid.

185 Decompose the substance by more or less protracted digestion with hydrochloric acid or nitric acid evaporate on the water-bath* to dryness (§ 140, II., *a*), and treat the residue, according to circumstances, with water, hydrochloric acid, or nitric acid; filter off the residuary silicic acid, and determine the other acids in the filtrate. In presence of boracic acid or fluorine this method is inapplicable, and the process described in *b* is employed instead. If carbonates are present, the carbonic acid is determined in a separate portion of the substance.

b. In Compounds which are not decomposed by Hydrochloric Acid.

186 Decompose the substance by fusion with carbonate of soda and potassa (§ 140, II., *b*, *α*), and either treat the residue at once cautiously with dilute hydrochloric or nitric acid, and the solution thus obtained as in *a*; or boil the residue with water, precipitate the dissolved silicic acid from the solution by heating with bicarbonate of ammonia, filter, and in the mixed residue and precipitate determine the silicic acid by treating with hydrochloric acid and proceeding as directed § 140, II., *a*., in the filtrate, determine the other acids. Which of these two methods may be preferable in particular cases, depends upon the nature of the bases, and upon the proportion which the silicic acid bears to the latter. In presence of boracic acid or fluorine, the latter method alone is applicable.

8. Carbonic Acid from all other Acids.

187 When carbonates are heated with stronger acids, the carbonic acid is expelled; the presence of carbonates, therefore, does not interfere with the estimation of most other acids. And as, on the other hand, the carbonic acid is determined by the loss of weight or by combination of the expelled gas, the presence of salts of non-volatile acids does not interfere with the determination of the carbonic acid. Accordingly, with compounds containing carbonates, sulphates, phosphates, &c., either the carbonic acid is determined in one portion and the other acids in another, or both estimations are performed on one portion. In the latter case the process described p. 293, *e*, may be used with advantage, the other acids being determined in the solution remaining in the decomposing flask. In presence of fluorides, one of the weak non-volatile acids, such as tartaric acid or citric acid, must be employed to expel the carbonic acid; since, were sulphuric acid or hydrochloric acid used for the purpose, part of the liberated hydrofluoric acid would escape with the carbonic acid. If, as will occasionally happen in an analysis, a mixed precipitate of fluoride of calcium and carbonate of lime is thrown down from a solution, the two salts may be separated by evaporating with acetic acid to dryness, and extracting the residue with water; the acetate of lime formed from the carbonate is dissolved, the fluoride of calcium is left behind.

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* A higher temperature would not answer.

SECOND GROUP.

HYDROCHLORIC ACID—HYDROBROMIC ACID—HYDRIODIC ACID—HYDROCYANIC ACID—HYDROSULPHURIC ACID.

I. SEPARATION OF THE ACIDS OF THE SECOND GROUP FROM THOSE OF THE FIRST.

§ 167.

a. All the Acids of the Second Group from those of the First.

Mix the dilute solution with nitric acid, add nitrate of silver in **188** excess, and filter off the insoluble chloride, bromide, iodide, &c., of silver. The filtrate contains the whole of the acids of the first group, the silver salts of these acids being soluble in water or in nitric acid. Carbonic acid must, under all circumstances, be determined in a separate portion. The estimation may be effected after § 139, *d*, or *e*. In the first case the remarks on p. 289 must be borne in mind.

b. Some of the Acids of the Second Group from Acids of the First Group.

As it is often inconvenient for the further separation of the acids **189** of the second group to have them all in the form of insoluble silver compounds, the analysis is sometimes effected by separating first the acid of the first group, then that of the second. If the quantity of disposable substance is large enough, the most convenient way generally is to determine the several acids—*e.g.*, sulphuric acid, phosphoric acid, chlorine, sulphuretted hydrogen, &c.—in separate portions.

Of the infinite number of combinations that may present themselves we will here consider only the most important.

1. SULPHURIC ACID may be readily separated from chlorine, bro- **190** mine, iodine, and cyanogen, by precipitation with a salt of baryta. If the acids of the second group are to be determined in the same

portion, nitrate of baryta or acetate of baryta is used instead of chloride of barium. In presence of sulphuretted hydrogen, sulphuric acid cannot be determined in this way, as part of the sulphuretted hydrogen would be converted into sulphuric acid by the oxygen of the air. The error thus introduced into the process may be very considerable (Fresenius*). The sulphuretted hydrogen must, therefore, first be removed by addition of chloride of copper, and the sulphuric acid determined in the filtrate; or, the sulphuretted hydrogen must be completely oxidized into sulphuric acid by chlorine, and a corresponding deduction afterwards made in calculating the quantity of the sulphuric acid.

2. Phosphoric Acid may be precipitated by means of nitrate of **191** magnesia and ammonia, after addition of nitrate of ammonia; oxalic acid by nitrate of lime; chlorine, bromine, iodine, &c., are determined in the filtrate.

3. Chlorine in Silicates.

a. If the silicates dissolve in dilute nitric acid, precipitate the **192** highly dilute solution with nitrate of silver, without applying heat; remove the excess of silver from the filtrate by dilute hydrochloric acid, still without applying heat; and then separate the silicic acid in the usual way.

b. If the silicate becomes gelatinous upon its decomposition with nitric acid, dilute, allow to deposit, filter, wash the separated silicic acid, and treat the filtrate as in *a.*

c. If nitric acid fails to decompose the silicates, mix the substance with carbonate of soda and potassa, moisten the mass with water, dry in the crucible, fuse, boil with water, remove the dissolved silicic acid by means of carbonate of ammonia and then precipitate, after addition of nitric acid, with nitrate of silver (H. Rose).

4. Chlorides in presence of Fluorides.

If the substance is soluble in water, the separation may be effected **193** as directed in **188**; but it is more convenient to precipitate the fluorine with nitrate of lime, and the chlorine in the filtrate with nitrate of silver. Insoluble compounds are fused with carbonate of soda and silicic acid.

5. Chlorine in presence of Fluorine in Silicates.

Proceed as directed **18'**. Saturate the alkaline filtrate nearly **194** with nitric acid, precipitate with nitrate of lime, separate the fluoride of calcium and the carbonate of lime as directed in **187**, and precipitate the chlorine in the filtrate by nitrate of silver.

6. Sulphides in Silicates.

If the substance is decomposable by acids, reduce it to the very **195** finest powder, and treat with fuming nitric acid free from sulphuric acid (§ 148 II., 2, *a*, p. 326). When the sulphur is completely oxidized, dilute, filter off the silicic acid, add carbonate of ammonia to the filtrate, to remove the portion of silicic acid which may possibly have dissolved; filter again, and determine in the filtrate the sulphuric acid formed. If, on the contrary, the substance is not decomposable by acids, fuse with 4 parts of carbonate of soda and 1 part of nitrate of potassa, boil the fused mass with water, filter, remove the dissolved silicic acid from the filtrate by carbonate of ammonia (**181**), filter again, and determine in the filtrate the sulphuric acid produced from the sulphur.

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* Journ. f. prakt. Chem. 70, 9.

Supplement.

ANALYSIS OF COMPOUNDS, CONTAINING SULPHIDES OF THE ALKALI METALS, AND ALKALINE CARBONATES, SULPHATES, AND HYPOSULPHITES.

§ 168.

196 The following method was first employed by G. WERTHER[*] in the examination of gunpowder residues.

Put the substance into a flask, add water, in which a sufficient quantity of carbonate of cadmium[†] is suspended; cork, and shake the vessel well. The sulphide of the alkali metal decomposes completely with the carbonate of cadmium. Filter the yellowish precipitate off, and treat it with dilute acetic acid (not with hydrochloric); the carbonate of cadmium dissolves, the sulphide of cadmium is left undissolved. Oxidize the latter with chlorate of potassa and nitric acid (p. 327), and precipitate with chloride of barium the sulphuric acid formed from the sulphide.

Heat the fluid filtered from the yellow precipitate, and mix with solution of neutral nitrate of silver. The precipitate thrown down by that reagent consists of carbonate of silver and sulphide of silver ($K\ O, S_2O_2 + Ag\ O, N\ O_5 = K\ O, S\ O_3 + Ag\ S + N\ O_5$). Remove the former salt by means of ammonia, and precipitate the silver from the ammoniacal solution—after acidifying with nitric acid—by means of chloride of sodium. Each 1 eq. chloride of silver so obtained corresponds to 1 eq. carbonate.[‡] Dissolve the sulphide of silver in dilute boiling nitric acid, determine the silver in the solution as chloride of silver, and calculate from the result the quantity of the hyposulphite; 1 eq. $Ag\ Cl$ corresponds to 2 eq. sulphur in hyposulphurous acid, and accordingly to 1 eq. hyposulphite ($K\ O, S_2O_2$).

From the fluid filtered from the sulphide and carbonate of silver remove first the excess of silver by means of hydrochloric acid, and then precipitate the sulphuric acid by a salt of baryta. From the sulphuric acid found you have, of course, to deduct the quantity of that acid resulting from the decomposition of the hyposulphurous acid, and accordingly for 1 part by weight of chloride of silver formed from the sulphide, 0·28 parts by weight of sulphuric acid. The difference gives the amount of sulphuric acid originally present in the analyzed compound. By way of control, you may determine, in the fluid filtered from the sulphate of baryta, the alkali as sulphate as directed in § 97 or § 98.

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[*] Journ. f. prakt. Chem. 55, 22.

[†] To obtain the carbonate of cadmium free from alkali, carbonate of ammonia must be used as precipitant.

[‡] A quantity equivalent to the sulphide found has to be deducted from this ($K\ S + Cd\ O, C\ O_2 = Cd\ S + K\ O, C\ O_2$).

II. SEPARATION OF THE ACIDS OF THE SECOND GROUP FROM EACH OTHER.

§ 169.

1. CHLORINE FROM BROMINE.

All the methods of direct analysis hitherto proposed to effect the separation of chlorine from bromine are defective. The bromine is therefore usually determined indirectly.

197 *a*. Precipitate with nitrate of silver, wash the precipitate, dry, fuse, and weigh. Transfer an aliquot part of the mixed chloride and bromide of silver to a light weighed bulb-tube,* fuse in the bulb, let the mass cool, and weigh. This operation gives both the total weight of the tube with its contents, and the weight of the portion of mixed chloride and bromide of silver in the bulb. The greatest accuracy in the several weighings is indispensable. Now transmit through the tube a slow stream of dry pure chlorine gas, heat the contents of the bulb to fusion, and shake the fused mass occasionally about in the bulb. After the lapse of about 20 minutes, take off the tube, allow it to cool, hold it in an oblique position, that the chlorine gas may be replaced by atmospheric air, and then weigh. Heat once more, for about 10 minutes, in a stream of chlorine gas, and weigh again. If the two last weighings agree, the experiment is terminated; if not, the operation must be repeated once more. The loss of weight suffered, multiplied by 4·2203 gives the quantity of the bromide of silver decomposed by the chlorine. For the proof of this rule see § 197.

This method gives very accurate results, if the proportion of bromine present is not too small; but most uncertain results in cases where mere traces of bromine have to be determined in presence of large quantities of chlorides, as for instance in salt-springs. To render the method available in such cases, the great point is to produce a silver compound containing all the bromine, and only a small part of the chlorine. This end may be attained in several ways. In these processes the quantity of chlorine is found by completely precipitating a separate portion with silver solution, and deducting the bromide of silver found from the weight of the precipitate.

α. Mix the solution with carbonate of soda in excess, filter if necessary, evaporate nearly to dryness, extract the residue with hot absolute alcohol; the solution contains the whole of the alkaline metallic bromide, and only a small portion of the alkaline metallic chloride; add a drop of soda solution, and evaporate; dissolve the residue in water, acidify with nitric acid, and precipitate with silver solution.

β. FEHLING'S method.†

198 Mix the solution *cold* with a quantity of solution of nitrate of silver not nearly sufficient to effect complete precipitation, shaking the mixture vigorously, and leave the precipitate for some time in the fluid, with repeated shaking. If the amount of the precipitate produced corresponds at all to the quantity of bromine present, the whole of the latter substance is obtained in the precipitate.

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* The best way of effecting the removal of the fused mass from the crucible is to fuse again, and then pour out.

† Journ. f. prakt. Chem. 45, 269.

FEHLING gives the following rule:—

If the fluid contains 0·1 % bromine, use $\frac{1}{5}$ or $\frac{1}{6}$ the quantity of solution of nitrate of silver that would be required to effect complete precipitation; if 0·01 %, $\frac{1}{10}$; if 0·002 %, $\frac{1}{30}$; if 0·001 %, $\frac{1}{60}$.

Wash the mixed precipitate of chloride and bromide of silver *thoroughly;* dry, ignite, weigh, and treat with chlorine, as above.

γ. MARCHAND[*] has slightly modified FEHLING's method. He **199**
reduces with zinc the mixed precipitate of chloride and bromide of silver obtained by FEHLING's fractional precipitation; decomposes the solution of chloride and bromide of zinc with carbonate of soda; evaporates to dryness, and extracts the residue with absolute alcohol, which dissolves all the bromide of sodium with only a little of the chloride of sodium; he then evaporates the solution to dryness, takes up the residue with water, precipitates again with solution of nitrate of silver, and subjects a part of the weighed precipitate to the treatment with chlorine.

δ. If a fluid containing chlorides in presence of some bromide, is heated, in a distillation flask, with hydrochloric acid and binoxide of manganese, the whole of the bromine passes over before any of the chlorine. Upon this circumstance, MOHR[†] bases the following method for effecting the concentration of bromine:—

Distil as stated, and conduct the vapors, through a doubly bent tube, into a wide WOULF's bottle, which contains some strong solution of ammonia. Dense fumes form in the bottle, filling it gradually. Conduct the excess of vapors from the first into a second bottle, with narrow neck, which contains ammoniated water. Both bottles must be sufficiently large to allow no vapors to escape. When the whole of the bromine is evolved, which may be distinctly seen by the color of the space above the liquid in the distillation flask and tubes, raise the cork of the flask to prevent the receding of bromide of ammonium fumes. Let the apparatus cool, and unite the contents of the two bottles; the fluid contains the whole of the bromine, with a relatively small portion of the chlorine.

b. Instead of treating the mixed chloride and bromide of silver **200**
in a current of chlorine as in *a*, it may also be reduced to metallic silver in a current of hydrogen. After accurately determining the weight of the reduced metal, calculate the amount of chloride of silver equivalent to it; subtract from this the weight of the chloride and bromide of silver subjected to the reducing process, and we have the same difference as served in *a* for the point of departure of the calculation (WACKENRODER). It will be seen that one and the same portion of mixed bromide and chloride of silver may be treated first as directed in *a*, then, by way of control, as directed in *b*. The difference found in the direct way in the first, and by calculation in the second experiment, between the weight of the mixed chloride and bromide of silver and the amount of chloride of silver equivalent to it, must be the same.

c. PISANI recommends to add a known quantity of solution of **201**
nitrate of silver in slight excess, filter, and determine the silver in

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[*] Journ. f. prakt. Chem. 47, 363.

[†] Annal. d. Chem. u. Pharm. 93, 80.

the filtrate by iodide of starch (p. 215). The precipitate is weighed as in *c.* This method precludes the partial precipitation.

202 *d.* Determine in a portion of the solution the chlorine + bromine (by precipitating with solution of silver), either gravimetrically or volumetrically; in another portion the bromine, either by the colorimetric method (§ 143, I., *c*), or by the volumetric method (§ 143, I., *b*). Calculate the chlorine from the difference. The method is very suitable for an expeditious analysis of mother-liquors.

2. Chlorine from Iodine.

203 *a.* Proceed exactly as for the indirect determination of bromine in presenec of chlorine (**197**). The loss of weight suffered by the silver precipitate in the fusion in chlorine gas, multiplied by 2·567, gives the quantity of the iodide of silver decomposed by chlorine. The methods described in **200** and **201**, may also be employed. The results obtained by these methods in the case of chlorine and iodine are still more accurate than in the case of chlorine and bromine, as the equivalents of iodine and chlorine differ far more widely than those of chlorine and bromine.

204 *b.* Add to the solution ½ c. c. of standard solution of iodide of starch (p. 215), then, drop by drop, with stirring, standard solution of silver (p. 304), until the iodide of starch is decolorized. The amount of silver solution used (after deducting the small quantity required for the decolorization of the ½ c. c. of iodide of starch solution added, and which must be separately determined) corresponds exactly to the amount of iodine in the analyzed compound; for iodide of starch is decolorized before the precipitation of chlorine begins. To determine now the chlorine also, add again solution of nitrate of silver in slight excess, filter, and determine the excess of silver in the filtrate by means of iodide of starch (p. 215). Deduct the amount of solution of nitrate of silver corresponding to the ½ c. c. of iodide of starch solution added, and to the iodine present, as well as the excess of silver solution from the total quantity added, and calculate the chlorine from the difference. This method is expeditious; the results are accurate (Pisani*). Compare also Expt. No. 94.

The following methods are especially adapted for the determination of small quantities of iodide in the presence of large quantities of chloride:—

205 *c.* Mix the solution with a few drops of solution of hyponitric acid in sulphuric acid, or with red fuming nitric acid, add 4 to 5 grm. bisulphite of carbon, shake violently, separate the violet-colored bisulphide from the fluid containing the chlorine (and bromine) by cautious decantation, and shake the decanted fluid with fresh bisulphide. After the violet bisulphide has been washed by decantation, the water being poured off through a filter, the iodine may be determined as follows: The solution should be in a stoppered bottle, covered with a layer of water. Add a dilute solution of hyposulphite of soda, with shaking, finally after addition of every two drops. The violet coloration gradually disappears. The end-point is easy to hit with perfect certainty. Now determine the value of the solution of hyposulphite, by shaking a few c. c. of standard iodine solution with bisulphide of carbon, and then adding hyposulphite to decoloration. Results good.

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* Compt. rend. 44, 352; Journ. f. prakt. Chem. 72, 266.

d. Precipitate a portion with silver solution and determine the **206** chlorine + iodine; in a second portion estimate the iodine volumetrically (§ 145, I., *c*, or *d*), and calculate the chlorine from the difference.

e. For technical purposes the following method is also suitable. It **207** was recommended by WALLACE and LAMONT* for the estimation of iodine in kelp. The kelp-lie is nearly neutralized with nitric acid, evaporated to dryness, and the residue fused in a platinum vessel to oxidation of all the sulphides. Treat with water, filter, add nitrate of silver till the precipitate appears perfectly white, wash, digest with strong ammonia, and weigh the residual iodide of silver. Finally, add to the weight of the latter the amount which passes into solution in the ammonia; it is $\frac{1}{2493}$ of the aqueous ammonia (sp. gr. 0·89) used.

3. CHLORINE, BROMINE, AND IODINE FROM EACH OTHER.

a. Determine in a portion of the compound the chlorine, bro- **208** mine and iodine, jointly by precipitation with nitrate of silver. Determine the silver in the weighed precipitate as in **200.** Or add a known quantity of solution of nitrate of silver in slight excess, filter, and determine the small excess of silver in the filtrate by means of iodide of starch (**201**).

Determine the iodine separately by DUPRÉ's method (see below), calculate the quantity of iodide of silver and of silver corresponding to the amount of iodine found, deduct the calculated amount of iodide of silver from the mixed iodide, chloride, and bromide of silver, that of the silver from the known quantity of the metal contained in the mixed compound; the remainders are respectively the joint amount of chloride and bromide of silver, and the quantity of the metal contained therein; these are the data for calculating the chlorine and bromine (**200**).

As regards the estimation of iodine in presence of bromides, A. and F. DUPRÉ found that if the solution of an iodide contains 1 part of bromide of potassium, or more, in 1500 parts of water, protobromide of iodine (I Br) is formed upon addition of chlorine water; if the solution contains less than 1 part of bromide of potassium in 1500 parts of water, higher bromides in varying proportions are formed in addition to the protobromide. If the solution contains only 1 part of bromide of potassium to 13000 parts of water, pentabromide of iodine alone is formed. If the iodine was dissolved in bisulphide of carbon, the conversion into I Br is marked simply by the change of the violet color of the fluid to yellowish brown (zirconium color), whereas the formation of $I\,Br_5$ is marked by the change of violet to white.

Upon these reactions A. and F. DUPRÉ have based the following method :—Test the fluid first by adding bisulphide of carbon, and then, gradually, chlorine water, to see whether the color will change from violet to white. If this is not the case, dilute to the required degree, and to make quite sure, add one-half more water; then proceed as directed § 145, I., *c*, α or β. A. and F. DUPRÉ obtained most satisfactory results by this process; the method is particularly recommended for the determination of small quantities of iodine in lies which contain large quantities of chlorides, and not too small quantities of bromides. If the latter are too small, exact results cannot be obtained by the indirect method, on which the bromine estimation is based. To determine bromine directly, we may, after adding a sufficient quantity of chlorine water to destroy the violet color of the bisulphide, and consequently to form $I\,Cl_5$, or, as the case may be, $I\,Br_5$ (6 eq. chlorine = 1 eq. iodine), add more chlorine water till the whole of the bromine is converted into Br Cl. 2 eq. of this second quantity of chlorine correspond to 1 eq. bromine (A. REIMANN). The details will be found § 143, I., *b*. To explain, I will suppose the case in which 5 eq. K Br and 1 eq. K I are present. $K\,I + 5\,K\,Br + 6\,Cl = 6\,K\,Cl + I\,Br_5$ and $I\,Br_5 + 10\,Cl = I\,Cl_5 + 5\,Br\,Cl$.

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* Chem. Gaz. 1859, 137.

b. Proceed generally as in *a*, but determine the iodine by PISANI'S method (**204**). This method also gives very satisfactory results, especially in the presence of large quantities of iodides. Presence of bromides does not interfere with the accuracy of the estimation of the iodine (Expt. No. 95). **209**

4. ANALYSIS OF IODINE CONTAINING CHLORINE.

a. Dissolve a weighed quantity of the dried iodine in cold sulphurous acid, precipitate with solution of nitrate of silver, digest the precipitate with nitric acid, to remove the sulphite of silver which may have coprecipitated, and weigh. The calculation of the iodine and chlorine is made by the following equations, in which *A* represents the quantity of iodine analyzed, *x* the iodine contained in it, *y* the chlorine contained in it, and *B* the amount of chloride and iodide of silver obtained:— **210**

$$x + y = A, \text{ and}$$

$$\frac{Ag + I}{I}x + \frac{Ag + Cl}{Cl}y = B$$

Now as

$$\frac{Ag + I}{I} = 1{\cdot}851$$

and

$$\frac{Ag + Cl}{Cl} = 4{\cdot}045$$

we have

$$y = \frac{B - 1{\cdot}851\,A}{2{\cdot}194}$$

b. If you have free iodine and free chlorine in solution, determine in one portion, after heating with sulphurous acid, the iodine as iodide of palladium (§ 145, I., *b*), and treat another portion as directed § 146, 1. Deduct from the apparent amount of iodine found by the latter process, the actual quantity calculated from the iodide **211** of palladium; the difference expresses the amount of iodine equivalent to the chloride contained in the substance.

5. Analysis of Bromine containing Chlorine.

a. Proceed exactly as in **210**, weighing the bromine in a small glass bulb. Taking A to be equal to the analyzed bromine, B to the bromide and chloride of silver obtained, x to the bromine contained in A, y to the chlorine contained in A, the calculation is made by the following equations:— **212**

$$x + y = A$$

and

$$y = \frac{B - 2{\cdot}35\,A}{1{\cdot}695}$$

b. Mix the weighed anhydrous bromine with solution of iodide of potassium in excess, and determine the separated iodine as directed § 146. **213**

From these data, the respective quantities of bromine and chlorine are calculated by the following equations. Let A represent the weighed bromine, i the iodine found, y the chlorine contained in A, x the bromine contained in A, then

$$x + y = A$$

$$y = \frac{i - 1{\cdot}5866\,A}{1{\cdot}991}$$

Bunsen, the originator of methods 4 and 5, has experimentally proved their accuracy.*

6. Cyanogen from Chlorine, Bromine, or Iodine.

a. Precipitate with solution of nitrate of silver, collect the precipitate upon a weighed filter, and dry in the water-bath until the weight remains constant; then determine the cyanogen by the method of organic analysis; the difference expresses the quantity of the chlorine, bromine, or iodine. **214**

b. Precipitate with solution of nitrate of silver as in *a*, dry the precipitate at 100°, and weigh. Heat the precipitate, or an aliquot part of it, in a porcelain crucible, with cautious agitation of the contents, to complete fusion; add dilute sulphuric acid to the fused mass, then reduce by zinc, filter the solution from the metallic silver and paracyanide of silver, and determine the chlorine, iodine, or bromine in the filtrate, in the usual way by solution of nitrate of silver. The cyanide of silver is the difference. Neubauer and Kerner † obtained very satisfactory results by this method. **215**

c. Determine the radicals jointly in a portion of the solution, by precipitating with solution of nitrate of silver, and the cyanogen in another portion, in the volumetric way (§ 147, I., *b*). **216**

7. Ferro- or Ferricyanogen from Hydrochloric Acid.

To analyse say ferro- or ferricyanide of potassium, mixed with the chloride of an alkali metal, determine in one portion the ferro- or ferricyanogen as directed § 147, II., *g*; acidify another portion with nitric acid, precipitate with solution of nitrate of silver, wash the **217** precipitate, fuse with 4 parts of carbonate of soda and 1 part of nitrate of potassa, extract the fused mass with water, and determine the chlorine in the solution as directed in § 141.

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* Annal d. Chem. u. Pharm. 86, 274, 276.

† Ibid. 101, 344.

8. Sulphuretted Hydrogen from Hydrochloric Acid.

218 The old method of separating the two acids by means of a metallic salt is liable to give false results, as part of the chloride of the metal may fall down with the sulphide. We therefore precipitate both as silver compounds, dry the precipitate at 100°, and determine the sulphur in a weighed portion; or—and this is usually preferred—determine in a portion of the solution the sulphuretted hydrogen as directed § 148, I, *a*, *b*, or *c*, in another portion the sulphur + chlorine in form of silver salts. If you employ a solution of nitrate of silver mixed with excess of ammonia, for the determination of the sulphuretted hydrogen, you may, after filtering off the sulphide of silver, estimate the chlorine directly as chloride of silver, by adding nitric acid, and, if necessary, more neutral silver solution. To remove sulphuretted hydrogen from an acid solution, in order that chlorine may be determined in the latter by means of nitrate of silver, H. Rose recommends to add solution of sulphate of sesquioxide of iron, which will effect the separation of sulphur alone; the separated sulphur is allowed to deposit, and then filtered off.

THIRD GROUP.

Nitric Acid—Chloric Acid.

I. Separation of the Acids of the Third Group from those of the first two Groups.

§ 170.

219 *a.* If you have a mixture of nitric acid or chloric acid with another free acid in a fluid containing no bases, determine in one portion the joint amount of the free acid, by the acidimetric method (see Special Part), in another portion the acid mixed with the chloric or nitric acid, and calculate the amount of either of the latter from the difference.

220 *b.* If you have to analyze a mixture of a nitrate or chlorate with some other salt, determine in one portion the nitric acid or chloric acid volumetrically (§ 149, II., *d*, α or β, or II., *e*, and § 150), or the nitric acid by § 149, II., *a*, β; and in another portion the other acid. I think I need hardly remark, that no substances must be present which would interfere with the application of these methods.

221 *c.* From the chlorides of those metals which form with phosphoric acid insoluble tribasic phosphates, the salts of the acids of the third group may be separated also by digesting the solution with recently precipitated thoroughly washed tribasic phosphate of silver in excess, and boiling the mixture. In this process the chlorides transpose with the phosphate—chloride of silver and phosphate of the metal with which the chlorine was originally combined being formed, which both separate, together with the excess of the phosphate of silver,

whilst the chlorates and nitrates remain in solution (CHENEVIX; LASSAIGNE*).

d. The estimation of an alkaline chlorate, in presence of a chloride, may be effected also as follows:—Take two portions of the substance, determine the chlorine by means of silver solution, in one directly, in the other after reduction of the chloric acid by cautious ignition or by nascent hydrogen (§ 150, II., *c*). Calculate the chloric acid from the difference in the precipitates of chloride of silver. **222**

II. SEPARATION OF THE ACIDS OF THE THIRD GROUP FROM EACH OTHER.

We have as yet no method to effect the direct separation of nitric acid from chloric acid; the only practicable way, therefore, is to determine the two acids jointly in a portion of the compound, by the method given p. 330, *d*, measuring the sesquioxide of iron remaining by Oudeman's method (p. 203), and bearing in mind that 12 eq. of iron, converted from proto- into sesquichloride, correspond to 1 eq. of chloric acid. In another portion estimate the chloric acid, by adding carbonate of soda in excess, evaporating to dryness, fusing the residue until the chlorate is completely converted into chloride, and then determining the chlorine in the latter; 1 eq. chloride of silver produced from this corresponds to 1 eq. chloric acid, provided there was no chloride originally present. **223**

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[*] Journ. de Pharm. 16, 289; Pharm. Centralbl. 1850, 121.

SECTION VI.

ORGANIC ANALYSIS.

§ 171.

ORGANIC compounds contain comparatively only few of the elements. A small number of them consist simply of 2 elements, viz.,

C and H;

the greater number contain 3 elements, viz., as a rule,

C, H, and O;

most of the rest 4 elements, viz., generally,

C, H, O, and N;

a small number 5 elements, viz.,

C, H, O, N, and S;

and a few, 6 elements, viz.,

C, H, O, N, S, and P.

This applies to all the natural organic compounds which have as yet come under our notice. But we may artificially prepare organic compounds containing other elements besides those enumerated; thus we know many organic substances, which contain chlorine, iodine, or bromine; others which contain arsenic, antimony, tin, zinc, platinum, iron, cobalt, &c.; and it is quite impossible to say which of the other elements may not be similarly capable of becoming more remote constituents of organic compounds (constituents of organic radicals).

With these compounds we must not confound those in which organic acids are combined with inorganic bases, or organic bases with inorganic acids, such as tartrate of lead, for instance, silicic ether, borate of morphia, &c.; since in such bodies any of the elements may of course occur.

Organic compounds may be analyzed either with a view simply to resolve them into their proximate constituents; thus, for instance, a gum-resin into resin, gum, and ethereal oil;—or the analysis may have for its object the determination of the ultimate constituents (the elements) of the substance. The simple resolution of organic compounds into their proximate constituents is effected by methods perfectly similar to those used in the analysis of inorganic compounds; that is, the operator endeavors to separate (by solvents, application of heat, &c.) the individual constituents from one another, either directly, or after having converted them into appropriate forms. We disregard here altogether this kind of organic analysis—of which the methods must be nearly as numerous and varied as the cases to which they are applied—and proceed at once to treat of the second kind, which may be called *the ultimate analysis of organic bodies.*

The ultimate analysis of organic bodies (*here termed simply, organic analysis*) has for its object, as stated above, the determination of the elements contained in organic substances. It teaches us how to isolate these elements or to convert them into compounds of known composition, to separate the new compounds formed from one another, and to calculate from their several weights, or volumes, the quantities of the elements. Organic analysis, therefore, is based upon the same principle upon which rest most of the methods of separating and determining inorganic compounds.

The conversion of most organic substances into distinctly characterized and readily separable products, the weights of which can be accurately determined, offers no great difficulties, and organic analysis is therefore usually one of the more easy tasks of analytical chemistry;—and as, from the limited number of the elements which constitute organic bodies, there is necessarily a great sameness in the products of their decomposition, the analytical process is always very similar, and a few methods suffice for all cases. It is principally ascribable to this latter circumstance that organic analysis has so speedily attained its present high degree of perfection:—the constant examination and improvement of a few methods by a great number of chemists could not fail to produce this result.

An organic analysis may have for its object either simply to ascertain the relative quantities of the constituent elements of a substance,—thus, for instance, woods may be analyzed to ascertain their heating power, fats to ascertain their illuminating power,—or to determine not only the relative quantities of the constituent elementary atoms, but also their absolute quantities, that is, to determine the number of equivalents of carbon, hydrogen, oxygen, &c., which constitute 1 equivalent of the analyzed compound. In scientific investigations we have invariably the latter object in view, although we are not yet able to achieve it in all cases. These two objects cannot well be attained by one operation; each requires a distinct process.

The methods by which we ascertain the proportions of the constituent elements of organic compounds, may be called collectively, *the ultimate analysis of organic bodies*, in a more restricted sense; whilst the methods which reveal to us the absolute number of elementary equivalents constituting the complex equivalent of the analyzed compound may be styled *the determination of the equivalents of organic bodies.*

The success of an organic analysis depends both upon the method and its execution. The latter requires patience, circumspection, and skill; whoever is moderately endowed with these gifts will soon become a proficient in this branch. The selection of the method depends upon the knowledge of the constituents of the substance, and the method selected may require certain modifications, according to the properties and state of aggregation of the same. Before we can proceed, therefore, to describe the various methods applicable in the different cases that may occur, we have first to occupy ourselves here with the means of testing organic bodies qualitatively.

I. QUALITATIVE EXAMINATION OF ORGANIC BODIES.

§ 172.

It is not necessary for the correct selection of the proper method, to know all the elements of an organic compound, since, for instance, the presence or absence of oxygen makes not the slightest difference to the method. But with regard to other elements, such as nitrogen, sulphur, phosphorus, chlorine, iodine, bromine, &c., and also the various metals, it is absolutely indispensable that the operator should know positively whether either of them is present. This may be ascertained in the following manner:—

1. *Testing for Nitrogen.*

Substances containing a tolerably large amount of nitrogen exhale upon combustion, or when intensely heated, the well-known smell of singed hair or feathers. No further test is required if this smell is distinctly perceptible; otherwise one of the following experiments is resorted to:—

a. The substance is mixed with hydrate of potassa in powder or with soda-lime (§ 66, 4), and the mixture heated in a test-tube. If the substance contains nitrogen, ammonia will be evolved, which may be readily detected by its odor and reaction, and by the formation of white fumes with volatile acids. Should these reactions fail to afford positive certainty, every doubt may be removed by the following experiment:—Heat a somewhat larger portion of the substance, in a short tube, with an excess of soda-lime, and conduct the products of the combustion into dilute hydrochloric acid; evaporate the acid on the water-bath, dissolve the residue in a little water, and mix the solution with bichloride of platinum and alcohol. Should no precipitate form, even after the lapse of some time, the substance may be considered free from nitrogen.

b. LASSAIGNE has proposed another method, which is based upon the property of potassium to form cyanide of potassium when ignited with a nitrogenous organic substance. The following is the best mode of performing the experiment:—

Heat the substance under examination, in a test-tube, with a small lump of potassium, and after the complete combustion of the potassium, treat the residue with a little water (cautiously); filter the solution, add 2 drops of solution of sulphate of protoxide of iron containing some sesquioxide, digest the mixture a short time, and add hydrochloric acid in excess. The formation of a blue or bluish-green precipitate or coloration proves the presence of nitrogen.

Both methods are delicate: *a* is the more commonly employed, and suffices in almost all cases; *b* does not answer so well in the case of alkaloids containing oxygen (*e.g.* morphia, brucia).

c. In organic substances containing oxides of nitrogen, the presence of nitrogen cannot be detected with certainty by either *a* or *b*, but it may be readily discovered by heating the substance in a tube, when red acid fumes, imparting a blue tint to iodide of starch paper, will be evolved, accompanied often by deflagration.

2. *Testing for Sulphur.*

a. Solid substances are fused with about 12 parts of pure hydrate of potassa, and six parts of nitrate of potassa. Or they are intimately mixed with some pure nitrate of potassa and carbonate of soda; nitrate of potassa is then heated to fusion in a porcelain crucible, and the mixture gradually added to the fusing mass. The mass is allowed to cool, then dissolved in water, and the solution tested with baryta, after acidifying with hydrochloric acid.

b. Fluids are treated with fuming nitric acid, or with a mixture of nitric acid and chlorate of potassa, at first in the cold, finally with application of heat; the solution is tested as in *a.*

c. As the methods *a* and *b* serve simply to indicate the presence of sulphur in a general way, but afford no information regarding the state or form in which that element may be present, I add here another method, which serves to detect only the sulphur in the non-oxidized state in organic compounds.

Boil the substance with strong solution of potassa and evaporate nearly to dryness. Dissolve the residue in a little water, and test by means of a polished surface of silver, or by nitroprusside of sodium, or by just acidifying the dilute solution with hydrochloric acid, and adding a few drops of a mixture of sesquichloride of iron and ferricyanide of potassium (see "Qual Anal." § 156).

3. *Testing for Phosphorus.*

The methods described in 2, *a* and *b*, may likewise serve for phosphorus. The solutions obtained are tested for phosphoric acid with sulphate of magnesia; or with sesquichloride of iron, with addition of acetate of soda; or with molybdate of ammonia (comp. "Qual. Anal."). In method *b*, the greater part of the excess of nitric acid must first be removed by evaporation.

4. *Testing for Inorganic Substances.*

A portion of the substance is heated on platinum foil, to see whether or not a residue remains. When acting upon difficultly combustible substances, the process may be accelerated by heating the spot which the substance occupies on the platinum foil to the most intense redness, by directing the flame of the blow-pipe upon it from below. The residue is then examined by the usual methods. That volatile metals in volatile organic compounds—*e.g.*, arsenic in kakodyl—cannot be detected by this method, need hardly be mentioned.

These preliminary experiments should never be omitted, since neglect in this respect may give rise to very great errors. Thus, for instance, taurin, a substance in which a large proportion of sulphur was afterwards found to exist, had originally the formula $C_4\ N\ H_7\ O_{10}$ assigned to it. The preliminary examination of organic substances for chlorine, bromine, and iodine is generally unnecessary, as these elements do not occur in native organic compounds; and as their presence in compounds artificially produced by the action of the halogens requires generally no further proof. Should it, however, be desirable to ascertain positively whether a substance does or does not contain chlorine, iodine, or bromine, this may be done by the methods given § 188.

II. Determination of the Elements in Organic Bodies.[*]

§ 173.

A. Analysis of Compounds which consist simply of Carbon and Hydrogen, or of Carbon, Hydrogen, and Oxygen.

The principle of the method which serves to effect the quantitative analysis of such compounds is exceedingly simple. The substance is

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[* For Prof. Warren's admirable methods we must refer to his original papers in Am. Journ. Sci., 2d ser., vol. 38, p. 387, vol. 41, p. 40, and vol. 42, p. 156.]

burned to carbonic acid and water; these products are separated from each other and weighed, and the carbon of the substance is calculated from the weight of the carbonic acid, the hydrogen from that of the water. If the sum of the carbon and hydrogen is equal to the original weight of the substance, the substance contains no oxygen; if it is less than the weight of the substance, the difference expresses the amount of oxygen present.

The combustion is effected either by igniting the organic substance with oxygenized bodies which readily part with their oxygen (oxide of copper, chromate of lead, &c.); or at the expense both of free and combined oxygen.

a. SOLID BODIES.

Combustion with Oxide of Copper.

§ 174.

I. APPARATUS AND PREPARATIONS REQUIRED FOR THE ANALYSIS.

1. THE SUBSTANCE.—This must be most finely pulverized and perfectly pure and dry;—for the method of drying, I refer to § 26.

2. A TUBE IN WHICH TO WEIGH THE SUBSTANCE, made of thin glass about 20 cm. long, and of 7 mm. internal diameter; one end of the tube is closed by fusion; the other, during the operation of weighing, is stopped with a smooth cork.

3. THE COMBUSTION TUBE.—A tube of difficultly fusible glass (potassa glass), about 2 mm. thick in the glass, 80 to 90 cm. in length, and from 12 to 14 mm. inner diameter, is softened in the middle before a glassblower's lamp, drawn out as represented in fig. 69, and finally apart at

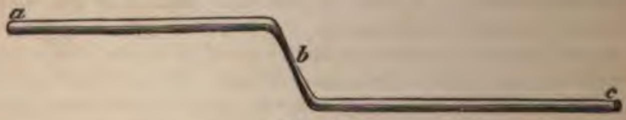

Fig. 69.

b. The fine points of the two pieces are then sealed and thickened a little in the flame, and the sharp edges of the open ends, *a* and *c*, are slightly rounded by fusion, care being taken to leave the aperture perfectly round. The posterior part of the tube should be shaped as shown in fig. 70, and not as in fig. 71.

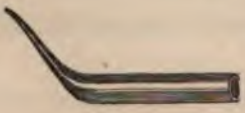

Fig. 70.

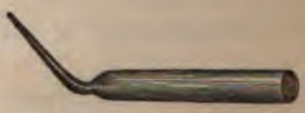

Fig. 71.

Two perfect combustion tubes are thus produced. The one intended for immediate use is cleaned with linen or paper attached to a piece of wire, and then thoroughly dried. This is effected either by laying the tube, with a piece of paper twisted over its mouth, for some time on a sand-bath, with occasional removal of the air from it by suction, with the aid of a glass tube, or (rapidly) by moving the tube to and fro over the flame of a gas or spirit lamp, heating its entire length, and continually removing the hot air by suction through the small glass tube (fig. 72).

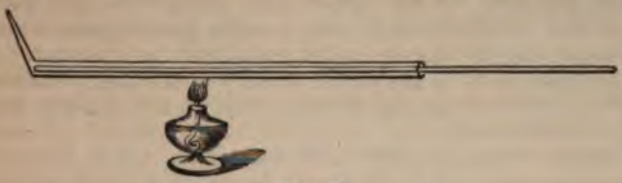

Fig. 72.

The combustion tube, when quite dry, is closed air-tight with a cork, and kept in a warm place until required for use.

In default of glass tubes possessed of the proper degree of infusibility, thin brass or copper foil, or brass gauze, is rolled round the tube, and iron wire coiled round it.

4. The Potash-bulbs (fig. 73).—This apparatus, devised by Liebig, is filled to the extent indicated in the engraving, with a clear solution of caustic potassa of 1·27 sp. gr. (§ 66, 6). The introduction of the solution of potassa into the apparatus is effected by plunging the end *a* into a beaker or dish into which a little of the solution has been poured out, and applying suction to *b*, by means of a caoutchouc tube. The two ends are then wiped perfectly dry with twisted slips of paper, and the outside of the apparatus with a clean cloth.

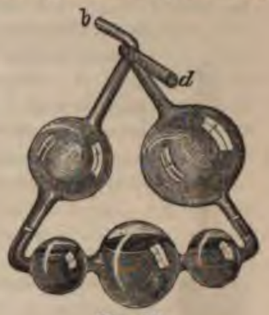

Fig. 73.

5. The Chloride-of-Calcium-tube (fig. 74) is filled in the following manner:—In the first place, the neck between the two bulbs of the tube is loosely stopped with a small cotton plug; this is effected by introducing a loose cotton plug into the wide tube, and applying a sudden and energetic suction at the other end. The large bulb is then filled with lumps of chloride of calcium (§ 66, 7, *b*), and the tube with smaller fragments, intermixed with coarse powder of the same substance; a loose cotton plug is then inserted, and the tube finally closed with a perforated cork, into which a small glass tube is fitted; the protruding part of the cork is cut off, and the cut surface covered over with sealing-wax; the edge of the little tube is slightly rounded by fusion.

In using this tube a considerable quantity of the water condenses in

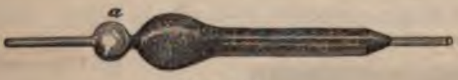

Fig. 74.

the empty bulb *a*, and at the close of the experiment may be poured out. The operator is thus enabled to test it as to reaction, &c., and also to use the same tube far oftener without fresh filling than he could otherwise.

6. A Small Tube of vulcanized India-rubber.—This must be so narrow that it can only be pushed with difficulty over the tube of the chloride of calcium tube on the one hand, and over the end of the potash bulbs on the other hand; in which case there is no need of binding with silk cord. If the rubber tube should be a little too wide, it must be tied round with silk cord, or with ignited piano wire. It is self-evident that the narrow end of the chloride of calcium tube should be of the same width as the tube *a* of the potash bulbs. The india-rubber tube is purified from any adherent sulphur, and dried in the water-bath previous to use.

7. Corks.—These should be soft and smooth, and as free as possible from visible pores. A cork should be selected which, after careful squeezing, fits perfectly tight, and screws with some difficulty to one-third of its length, at the most, into the mouth of the combustion-tube; a perfectly smooth and round hole, into which the end *a* of the chloride of calcium tube must fit perfectly air-tight, is then carefully bored through the axis of the cork. The cork is then kept for an hour or two in the water-bath. It is advisable always to have two corks of this description ready. Instead of ordinary corks, caoutchouc stoppers may be used with great advantage.

8. Oxide of Copper.—A Hessian crucible, of about 100 c. c. capacity, is nearly filled with oxide of copper prepared as directed in § 66, 1; the crucible is covered with a well-fitting overlapping lid, and heated to dull redness with charcoal, or in a suitable gas-furnace; it is then allowed to cool, so that by the time the oxide of copper is required for use, the hand can only just bear contact with it.

9. A wide glass Tube sealed at one end, or a Flask (fig. 75), in which the freshly ignited oxide of copper is allowed to cool, and from which it is transferred to the combustion tube, secure from the possible absorption of moisture from the air.

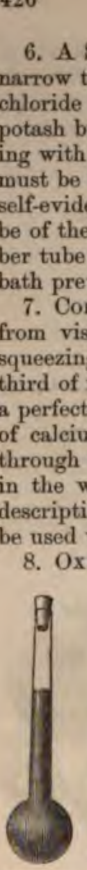
Fig. 75.

The freshly ignited and still quite hot oxide of copper is transferred direct from the crucible to this filling tube, or flask, which is then closed air-tight with a cork. It saves time to fill in at once a sufficient quantity of oxide to last for several analyses. If the cork fits tight, the contents will remain several days fit for use, even though a portion has been taken out, and the tube repeatedly opened.

10. A Mixing Wire of copper (fig. 76) with ring at one end for a handle, and a single corkscrew turn at the other, which should taper smoothly to a point.

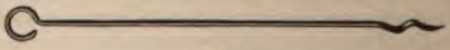
Fig. 76.

11. A Combustion-furnace.—Some time ago the only one used was Liebig's, in which charcoal is the fuel. Recently gas combustion furnaces have been introduced into most laboratories, because they are more cleanly and convenient.

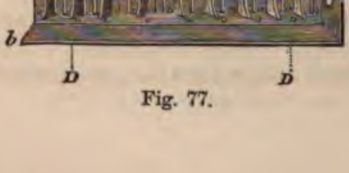

Fig. 77.

a. LIEBIG's combustion furnace is of sheet iron. It has the form of a long box, open at the top and behind. It serves to heat the combustion tube with red-hot charcoal. Fig. 77 represents the furnace as seen from the top.

It is from 50 to 60 cm. long, and from 7 to 8 deep; the bottom, which, by cutting small slits in the sheet iron, is converted into a grating, has a width of about 7 cm. The side walls are inclined slightly outward, so that at the top they stand about 12 cm. apart. A series of upright pieces of strong sheet iron, having the form shown in *D*, fig. 78, and riveted on the bottom of the furnace at intervals of about 5 cm., serves to support the combustion tube. They must be of exactly corresponding height with the round aperture in the front piece of the furnace (fig. 78, *A*).

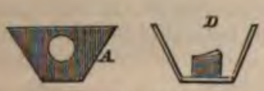

Fig. 78.

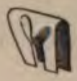

Fig. 79.

This aperture must be sufficiently large to admit the combustion tube easily. Of the two screens, the one has the form shown in fig. 79, the other that shown in fig. 78, *A*, with the border turned down at the upper edge. The openings cut into the screens must be sufficiently large to receive the combustion tube without difficulty. The furnace is placed upon two bricks resting upon a flat surface, and is slightly raised at the farther end, by inserting a piece of wood between the supports (see fig. 82). The apertures of the grating at the anterior end of the furnace must not be blocked up by the supporting bricks. In cases where the combustion tubes are of a good quality, the furnace may be raised by introducing a little iron rod between the furnace and the supporting brick. Placing the tube in a gutter of Russia sheet iron tends greatly to preserve it, but contact of the glass and iron must be prevented by an intervening layer of asbestos.

b. Gas combustion furnaces of the most various descriptions have been proposed. See § 178.

§ 175.

II. PERFORMANCE OF THE ANALYTICAL PROCESS.

a. Weigh first the potash apparatus, then the chloride of calcium tube. Introduce about 0·35—0·6 grm. of the substance under examination (more or less, according as it is rich or poor in oxygen) into the weighing tube,* which must be no longer warm, and weigh the latter accurately with its contents. The weight of the empty tube being approximately known, it is easy to take the right quantity of substance required for the analysis. Close the tube then with a smooth cork.

b. The filling of the combustion tube is effected as follows:—The perfectly dry tube is rinsed with some oxide of copper; a layer of oxide of copper, about 13 cm. long, is introduced into the posterior end of the combustion tube, by inserting the latter into the filling tube or flask containing the oxide of copper (fig. 80), holding both tubes in an oblique direction, and giving a few gentle taps.

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* Care must be taken that no particles of the substance adhere to the sides of the tube, at least not at the top.

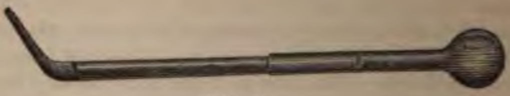

Fig. 80.

From the tube containing the substance remove the cork cautiously, to prevent the slightest loss of substance; insert the open end of the tube as deep as possible into the combustion tube, and pour from it the requisite quantity of substance by giving it a few turns, pressing the rim all the while gently against the upper side of the combustion tube, to prevent its coming into contact with the powder already poured out; the two tubes are, in this manipulation, held slightly inclined (see fig. 81).

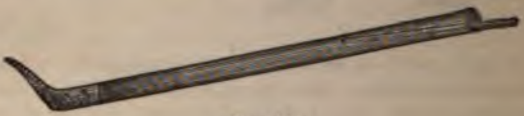

Fig. 81.

When a sufficient quantity of the substance has been thus transferred from the weighing to the combustion tube, the latter is restored to the horizontal position, which gives to the former a gentle inclination with the closed end downwards. If the little tube is now slowly withdrawn, with a few turns, the powder near the border of the opening falls back into it, leaving the opening free for the cork. The tube is then immediately corked and weighed, the combustion tube also being meanwhile kept closed with a cork. The difference between the two weighings shows the quantity of substance transferred from the weighing to the combustion tube. The latter is then again opened, and a quantity of oxide of copper, equal to the first, transferred to it from the filling tube, or flask, taking care to rinse down with this the particles of the substance still adhering to the sides of the tube. There is now in the hind part of the tube a layer of oxide of copper, about 25 cm. long, with the substance in the middle.

The next operation is the mixing: this is performed with the aid of the wire (fig. 76), which is pushed down to within 3 to 4 cm. of the end, and rapidly moved about in all directions until the mixture is complete and uniform, the tube being held nearly horizontal.

Oxide of copper is then poured in to within 5 to 6 cm. of the open end, and the tube is corked.

c. A few gentle taps on the table will generally suffice to shake together the contents of the tube, so as to completely clear the tail from oxide of copper, and leave a free passage for the evolved gases from end to end. Should this fail, as will occasionally happen, owing to malformation of the tail, the object in view may be attained by striking the mouth of the tube several times against the side of a table.

d. Connect the end *b* (fig. 82) of the weighed chloride of calcium tube with the combustion tube by means of a dried perforated cork, lay the furnace upon its supports, with a slight inclination forward, and place the combustion tube in it; connect the end B of the chloride of calcium tube, by means of a vulcanized india-rubber tube, with the end m of the potash apparatus, and, if necessary, secure the connection with silk cord, taking care to press the joint of the two thumbs close together whilst tightening the cords, since otherwise, should one of the cords happen to give way, the whole apparatus might be broken. Rest the potash apparatus upon a folded piece of cloth. Fig. 82 shows the whole arrangement.

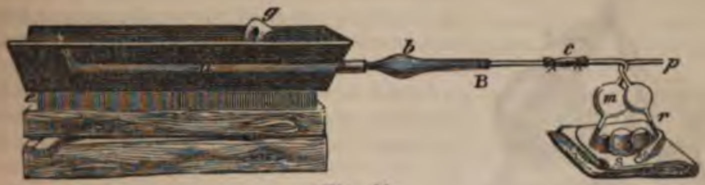

Fig. 82.

e. To ascertain whether the joinings of the apparatus fit air-tight, put a piece of wood about the thickness of a finger (s), or a cork or other body of the kind, under the bulb r of the potash apparatus, so as to raise that bulb slightly (see fig. 82). Heat the bulb m, by holding a piece of red-hot charcoal near it, until a certain amount of air is driven out of the apparatus; then remove the piece of wood (s), and allow the bulb m to cool. The solution of potassa will now rise into the bulb m, filling it more or less; if the liquid in m preserves, for the space of a few minutes, the same level which it has assumed after the perfect cooling of the bulb, the joinings may be considered perfect; should the fluid, on the other hand, gradually regain its original level in both limbs of the apparatus, this is a positive proof that the joinings are not air-tight. (The few minutes which elapse between the two observations may be advantageously employed in reweighing the little tube in which the substance intended for analysis was originally weighed.)

f. Let the mouth of the combustion tube project a full inch beyond the furnace; suspend the single screen over the anterior end of the furnace, as a protection to the cork; put the double screen over the combustion tube about two inches farther on (see fig. 82), replace the little piece of wood (s) under r, and put small pieces of red-hot charcoal first under that portion of the tube which is separated by the screen; surround this portion gradually altogether with ignited charcoal, and let it get red-hot; then shift the screen an inch farther back, surround the newly exposed portion of the tube also with ignited charcoal, and let it get red-hot; and proceed in this manner slowly and gradually extending the application of heat to the tail of the tube, taking care to wait always until the last exposed portion is red-hot before shifting the screen, and also to maintain the whole of the exposed portion of the tube before the screen in a state of ignition, and the projecting part of it so hot that the fingers can hardly bear the shortest contact with it. The whole process requires generally from $\frac{3}{4}$ to 1 hour. It is quite superfluous, and even injudicious, to fan the charcoal constantly;—this should be done however when the process is drawing to an end, as we shall immediately have occasion to notice.

The liquid in the potash bulbs is gradully displaced from the bulb *m* upon the application of heat to the anterior portion of the combustion tube, owing simply to the expansion of the heated air. The evolution of gas proceeds with greater briskness when the heat begins to reach the actual mixture; the first bubbles are only partly absorbed, as the carbonic acid contains still an admixture of air; but those which follow are so completely absorbed by the potassa, that a solitary air-bubble only escapes from time to time through the liquid. The process should be conducted in a manner to make the gas-bubbles follow each other at intervals of from $\frac{1}{2}$ to 1 second. Fig. 83 shows the proper position of the potash bulbs during the operation.

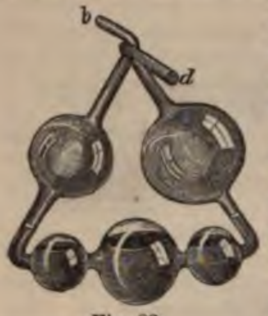

Fig. 83.

It will be seen from this that an air-bubble entering through *m* passes first into the bulb *b*, thence to *c*, from *c* to *d*, and passing over the solution in the latter, escapes finally into the bulb *f*, through the fluid which just covers the mouth of the tube *e*.

g. When the tube is in its whole length surrounded with red-hot charcoal, and the evolution of gas has relaxed, fan the burning charcoal gently with a piece of pasteboard. When the evolution of gas has entirely ceased, adjust the position of the potash bulbs to a level, remove the charcoal from the farther end of the tube, and place the screen before the tail. The ensuing cooling of the tube on the one hand, and the absorption of the carbonic acid in the potash bulbs on the other, cause the solution of potassa in the latter to recede, slowly at first, but with increased rapidity from the moment the liquid reaches the bulb *m*. (If you have taken care to adjust the position of the potash bulbs correctly, you need not fear that the contents of the latter will recede to the chloride of calcium tube.) When the bulb *m* is about half filled with solution of potassa, break off the point of the combustion tube with a pair of pliers or scissors, whereupon the fluid in the potash bulbs will immediately resume its level. Restore the potash bulbs now again to their original oblique position, join a caoutchouc tube to the potash bulbs, and slowly apply suction until the last bubbles no longer diminish in size in passing through the latter. It is better to employ a small aspirator instead of sucking with the mouth. You then know the volume of air that has passed through the apparatus.

This terminates the analytical process. Disconnect the potash bulbs and remove the chloride of calcium tube, together with the cork, which must not be charred, from the combustion tube; remove the cork also from the chloride of calcium tube, and place the latter upright, with the bulb upwards. After the lapse of half an hour, weigh the potash bulbs and the chloride of calcium tube, and then calculate the results obtained. They are generally very satisfactory. As regards the carbon, they are rather somewhat too low (about 0·1 per cent.) than too high. The carbon determination, indeed, is not free from sources of error; but none of these interfere materially with the accuracy of the results, and the deficiency arising from the one is partially balanced by the excess arising from the other. In the first place, the air which passes through the solution of potassa during the combustion, and finally during the process of suction, carries away with it a minute amount of moisture. The loss arising from this cause is increased if the evolution of gas proceeds very briskly, since this tends to heat the solution of potassa; and also if nitrogen or oxygen passes through the potash bulbs (compare § 176 and § 178). This may be remedied, however, by fixing to the exit end of the latter a tube with solid hydrate of potassa or soda-lime, the bulbs and this tube being always weighed together. In the second place, traces of carbonic acid from the atmosphere are carried into the potash apparatus in the final process of suction; this may be remedied by connecting the tail of the combustion tube, during the operation, with a tube containing hydrate of potassa by means of a perforated cork or flexible tube. In the third place, it happens frequently, in the analysis of substances containing a considerable proportion of water or of hydrogen, that the carbonic acid is not absolutely dried in passing through the chloride of calcium tube; this may be remedied by fixing behind the chloride of calcium tube, a tube filled with asbestos moistened with sulphuric acid.

Finally, if the mixture was not sufficiently intimate, traces of carbon remain unconsumed. It is therefore better to complete the combustion in oxygen gas. See below.

As regards the hydrogen, the results are very accurate, if the filling is skilfully performed with dry oxide of copper.

§ 176.

[*Completion of the Combustion by Oxygen Gas.* To insure the oxidation of the last traces of carbon and to leave the oxide of copper ready for use again, it is advisable to finish the combustion in a stream of oxygen. For this purpose the tail of the combustion tube must be made rather stout and long. When the potash-lye recedes, slip tightly over the suitably cooled tail a caoutchouc tube connected with a source of pure and dry oxygen gas, nip off the tip within this tube by help of a pliers, and cautiously let on the oxygen until the reduced copper is oxidized and the gas traverses the potash-bulbs. Then replace the stream of oxygen by one of pure and dry air, to remove all oxygen from the bulbs. To prevent loss by evaporation from the potash-lye, append to the potash-bulb a small tube of fragments of caustic potash, or employ Mulder's absorption apparatus, fig. 90, § 182.

The oxygen may be supplied from a gasometer, as shown fig. 84, § 178, or from a small tube-retort of fused chlorate of potassa. This method and that of § 175 are not applicable to organic salts of the alkalies or alkali-earths, since these bases retain a portion of carbonic acid.]

COMBUSTION WITH CHROMATE OF LEAD, OR WITH CHROMATE OF LEAD AND BICHROMATE OF POTASSA.

§ 177.

This method is especially resorted to in the analysis of salts of organic acids with alkalies or alkaline earths (as the chromic acid completely displaces carbonic acid from their bases), and of bodies containing sulphur, chlorine, bromine, or iodine.

Of the apparatus, &c., enumerated in § 174, all are required except oxide of copper, which is here replaced by chromate of lead (§ 66, 2). A narrow combustion tube may be selected, as chromate of lead contains a much larger amount of available oxygen in an equal volume than oxide of copper. A quantity of the chromate, more than sufficient to fill the combustion tube, is heated in a platinum or porcelain dish over a gas or BERZELIUS lamp, until it begins to turn brown; before filling it into the tube, it is allowed to cool down to 100°; and even below. The process is conducted as the one described in § 174.

One of the principal advantages which chromate of lead has over oxide of copper as an oxidizing agent being its property of fusing at a high heat, the temperature must, in the last stage of the process of combustion, be raised (by fanning the charcoal, &c.) sufficiently high to fuse the contents of the tube completely, as far as the substance extends. To heat the *anterior* end of the tube to the same degree of intensity would be injudicious, since the chromate of lead in that part would thereby lose all porosity, and thus also the power of effecting the combustion of the products of decomposition which may have escaped oxidation in the other parts of the tube.

As the chromate of lead, even in powder, is, on account of its density, by no means all that could be desired in this latter respect, it is preferable to fill the anterior part of the tube, instead of with chromate of lead, with coarsely pulverized strongly ignited oxide of copper, or with copper turnings which have been superficially oxidized by ignition in a muffle or in a crucible with access of air.

In the case of very difficultly combustible substances—*e.g.*, graphite—it is desirable that the mass should not only readily cake, but also, in the last stage of the process, give out a little more oxygen than is given out by chromate of lead. It is therefore advisable in such cases to add to the latter one-eighth of its weight of fused and powdered bichromate of potassa. With the aid of this addition, complete oxidation of even very difficultly combustible bodies may be effected (LIEBIG).

3. COMBUSTION WITH OXIDE OF COPPER IN A STREAM OF OXYGEN GAS.

§ 178.

Many chemists effect combustion with oxide of copper in a stream of oxygen supplied by a gasometer. The methods based upon this principle are employed not only for the analysis of difficultly combustible bodies, but also to effect the determination of the carbon and hydrogen in organic substances in general.

These methods require a gasometer filled with oxygen, and another with air, together with certain arrangements to dry the oxygen and air completely, and to free them from carbonic acid. They are resorted to in cases where a number of ultimate analyses have to be made in succession; and also more particularly in the analysis of substances which cannot be reduced to powder, and do not admit therefore of intimate mixture with oxide of copper, &c.

The heating may be effected with the charcoal combustion furnace (fig. 77, p. 426), but a gas furnace is most convenient.

Many forms of gas-furnace have been employed. One of the best is represented in fig. 84. The combustion tube rests in a gutter of sheet iron, but the glass is kept from contact with the metal by a layer of asbestos. It is well to secure the tube to the gutter by binding wire. At its anterior end the combustion tube is connected with a chloride of calcium tube and potash-bulb as usual. It is also necessary to have a third tube to collect traces of moisture which the current of hot gases might carry over from the potash solution. This tube *i* is filled with small fragments of caustic potash.

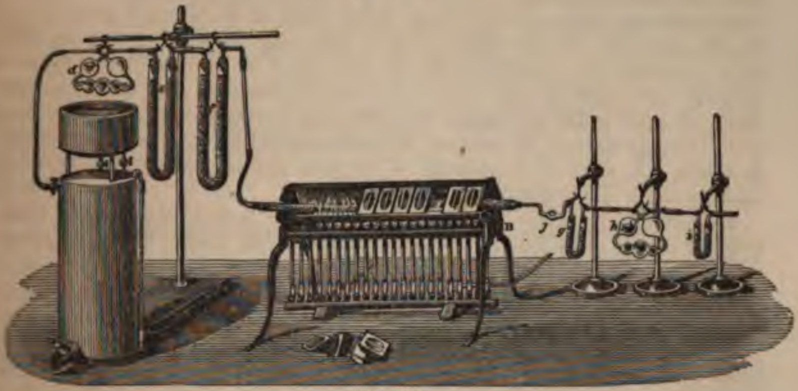

Fig. 84.

Posteriorly, the combustion tube is joined by a cork or caoutchouc stopper to a narrow glass tube which connects it with the gasometer and the apparatus for drying the oxygen. The gas on leaving the gasometer streams first through a potash bulb-tube *d*, then through a long U-tube, *e*, filled with chloride of calcium, and finally through the U-tube *f*, containing pumice saturated with oil of vitriol. It is well to attach a lever of a foot or so in length to the handle of the cock by which the supply of gas is admitted to the combustion tube, as thus the flow of oxygen is more easily regulated.

a. The ignition of the oxide of copper is effected in the tube. To accomplish this, a plug of asbestos is inserted into the anterior end, the tube being then filled to two-thirds of its length with oxide of copper; the posterior orifice is then joined to the drying apparatus interposed between the gasometer and the combustion tube, and the tube heated to gentle redness in its whole length, whilst a slow current of atmospheric air is conducted through it.* After complete ignition has been effected the fire is extinguished, the anterior end of the combustion tube, which up to this time has remained open, is connected with an unweighed chloride of calcium tube, and the ignited oxide allowed to cool in a slow stream of atmospheric air. When the tube is cold, it is opened at the posterior end, the substance introduced into it with the aid of a long tube (compare § 174), and quickly mixed with the oxide by means of a copper wire with twisted end (see fig. 76, p. 174); the after-part of the tube is filled to within 12 cm. with ignited oxide of copper, cooled in the tube or flask shown in fig. 75, p. 174; a few gentle taps on the table will suffice to shake the contents down a little, leaving a clear passage above. The posterior end of the tube is then again connected with *f*, and the chloride of calcium tube, affixed to the front of the combustion tube during the cooling, exchanged for the one which is accurately weighed, and to which the weighed tubes, *h* and *i*, are also joined.

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* [Either from a second gasometer, or by aid of an aspirator.]

The cock of the oxygen gasometer is now opened a little, so that the gas may pass in a very slow current through the apparatus; the cock is then suddenly turned off, and the level of the fluid in the two bulb tubes watched some time; if no change takes place in it, this is a proof that all the joinings are air-tight. After this, the anterior portion of the tube is heated to redness, as far as the layer of pure oxide of copper extends; the same is then done with the farther part also, as far as the layer of pure oxide of copper extends, the corks at both ends of the tube being protected by screens, as well as also the part containing the mixture. A very slow current of oxygen gas is transmitted all the time through the apparatus.

The part of the tube containing the mixture is then also heated, proceeding slowly from the anterior to the posterior part. The stream of oxygen gas is gradually increased, but never to an extent to allow the oxygen to escape through the potash bulbs *h*. When the tube in its whole length is at a red heat, and the evolution of gas has ceased, the cock is opened a little wider, and the transmission of oxygen continued, until at last, when the reduced oxide of copper is completely reoxidized, the gas begins to escape unabsorbed through the potash bulbs. The cock of the oxygen gasometer is now shut, whilst that of the air gasometer is opened a little; the combustion tube, &c., are allowed to cool in a slow stream of atmospheric air. The chloride of calcium tube, and the potash bulbs with the potassa tube joined to them, are then weighed.

A very great advantage of this method consists in this, that the combustion tube, after the termination of the first, is quite ready for a second analysis.

b. The combustion of most substances may be effected also without mixing with oxide of copper, by introducing the sample into a platinum, copper, or porcelain boat or tray (fig. 85). This method affords the advantage of enabling the operator to determine at the same time any unconsumed residue (ash) that may remain behind, which in some cases—in the analysis of coals, for instance—is a great convenience. The substance is weighed in the boat, enclosed in a corked glass tube.

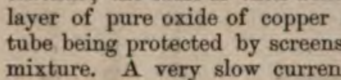

Fig. 85.

The process of combustion is then conducted as follows:—Introduce into the anterior end of the tube a plug of asbestos, then fill the tube with oxide of copper, leaving about 20 cm. free, and keep the oxide in its place by pushing an asbestos plug down upon it. Heat the tube now to redness in the combustion furnace, pass a current of air through it, to remove all moisture, connect the anterior end with an unweighed chloride of calcium tube, and let the apparatus cool; then push the boat containing the sample down to the rear asbestos plug, and connect the after-part of the tube with the purifying apparatus interposed between the gasometer and the combustion tube, the fore-part with the weighed chloride of calcium tube and potash bulbs with potassa tube. Heat the oxide of copper in the combustion tube to redness, and when approaching the part where the boat is placed, open the cock of the oxygen gasometer a little; when the heat has reached the contents of the boat, proceed with proper caution, and take care to pass neither too little nor too much oxygen through the tube. Increase the current of oxygen a little at last, and let the apparatus finally cool in a slow current of atmospheric air.

With this method, it is still easier than with *a* to use the combustion tube for a second analysis immediately after the first, as all that is required for the purpose is to insert a fresh boat with another sample of substance, to replace the one just removed.

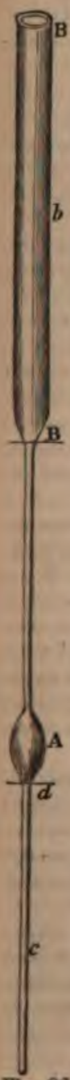

Fig. 86.

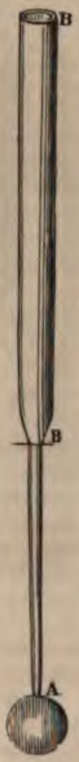

Fig. 87.

Volatile Substances, or Bodies undergoing Alteration at 100° (*losing Water, for instance*).

§ 179.

The process is conducted either according to § 174, or as directed § 178. Ignited chromate of lead, cooled in a closed tube, may also be employed as oxidizing agent.

b. Fluid Bodies.

α. Volatile liquids (*e.g.*, ethereal oils, alcohol, &c.).

§ 180.

1. The analysis of organic volatile fluids requires the objects enumerated in § 174. The combustion tube should be somewhat longer than there mentioned; it should have a length of 50 or 60 cm., according as the substance is less or more volatile. The process requires besides several small glass bulbs for the reception of the liquid to be analyzed. These bulbs are made in the following manner:—

A glass tube, about 30 cm. long and about 8 mm. wide, is drawn out as shown in fig. 86, fused off at *d*, and *A* expanded into a bulb, as shown in fig. 87. The bulbed part is then cut off at *β*. Another bulb is then made in the same way, and a third and fourth, &c., as long as sufficient length of tube is left to secure the bulb from being reached by the moisture of the mouth.

Two of these bulbs are accurately weighed; they are then filled with the liquid to be analyzed, closed by fusion, and weighed again. The filling is effected by slightly heating the bulb over a lamp and immersing the point into the liquid to be analyzed, part of which will now, upon cooling, enter the bulb. If the fluid is highly volatile, the portion entering the still warm bulb is converted into vapor, which expels the fluid again; but the moment the vapor is recondensed, the bulb fills the more completely. If the liquid is of a less volatile nature, a small portion only will enter at first; in such cases the bulb is heated again, to convert what has entered into vapor, and the point is then again immersed into the fluid, which will now readily enter and fill the bulb. The excess of fluid is ejected from the neck of the little tube by a sudden jerk; the point of the capillary neck is then sealed in the blowpipe flame. The combustion tube is now prepared for the process by introducing into it from the filling-tube or flask (§ 174), a layer of oxide of copper occupying about 6 cm. in length. The middle of the neck of one of the bulbs is slightly scratched with a file, the pointed end is quickly broken off, and the bulb and end are dropped into the combustion tube (see fig. 88). Another layer of oxide of copper, about 6—9 cm. long, is then filled in, and the other bulb introduced in the same manner as the first. The tube is finally nearly filled with oxide of copper. A few gentle taps upon the table suffice to clear a free passage for the gases evolved. (It is advisable to place in the anterior half of the combustion tube small lumps of oxide of copper [comp. § 66, 1], or superficially oxidized copper turnings, which will permit the free passage of the gases, even with a narrow channel, or no channel at all; since with a wide channel there is the risk of vapors passing unconsumed through the tube.)

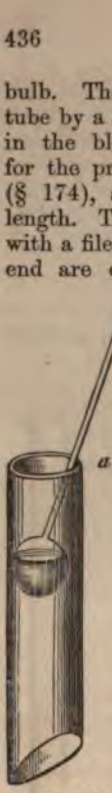

Fig. 88.

The combustion of highly volatile substances demands great care, and requires certain modifications of the common method. The operation commences by heating to redness the anterior half of the tube, which is separated from the rest by a screen, or in the case of highly volatile substances, by two screens; ignited charcoal is then placed behind the tube to heat the tail and prevent the condensation of vapor in that part. A piece of red-hot charcoal is now applied to that part of the tube which is occupied by the first bulb; this causes the efflux and evaporation of the contents of the latter; the vapor passing over the oxide of copper suffers combustion, and thus the evolution of gas commences, which is then maintained by heating very gradually the first, and after this the second bulb; it is better to conduct the operation too slowly than too quickly. Sudden heating of the bulbs would at once cause such an impetuous rush of gas as to eject the fluid from the potash bulbs. The tube is finally in its entire length surrounded with ignited charcoal, and the rest of the operation conducted in the usual way. If the air drawn through the apparatus tastes of the analyzed substance, this is a sure sign that complete combustion has not been effected.

2. In the combustion of liquids of high boiling point and abounding in carbon, *e.g.*, ethereal oils, unconsumed carbon is apt to deposit on the completely reduced copper near the substance; it is therefore advisable to distribute the quantity intended for analysis (about 0·4 grm.) in 3 bulbs, separated from each other in the tube by layers of oxide of copper.

3. In the combustion of less volatile liquids, it is advisable to empty the bulbs of their contents before the combustion begins: this is effected by connecting the filled tube with an exhausting syringe, and rarefying the air in the tube by a single pull of the handle; this will suffice to expand the air-bubble in each bulb sufficiently to eject the oily liquid from it, which is then absorbed by the oxide of copper.

4. If there is reason to apprehend that the oxide of copper may not

suffice to effect the complete combustion of the carbon, the process is terminated in a stream of oxygen gas (compare § 176).

5. If it is intended to effect the combustion in the apparatus described in § 178 (in a current of oxygen gas), the bulb must be drawn out to a fine long point, and filled almost completely with the fluid. The point is then sealed in the blowpipe flame, and the bulbs are transferred in that state to the combustion tube. When the anterior and the farther end of the tube are red-hot, a piece of ignited charcoal is put to the part occupied by the first bulb, when the expansion of the liquid will cause it to burst. When the contents of the first bulb are consumed, the second, and after this the third, are treated in the same way. This method will not answer, however, for very volatile liquids, as, *e.g.*, ether, on account of the explosion which would inevitably take place.

β. *Non-volatile Liquids* (*e.g.*, fatty oils).

§ 181.

The combustion of non-volatile liquids is effected either, 1, with chromate of lead, or oxide of copper and oxygen; 2, in the apparatus described § 178.

1. The operation is conducted in general as directed § 175 or § 176. The substance is weighed in a small tube, placed for that purpose in a tin foot (see fig. 89), and the mixing effected as follows:—Introduce into the combustion tube first a layer, about 6 cm. long, of chromate of lead, or of oxide of copper; then drop in the small cylinder with the substance, and let the oil completely run out into the tube; make it spread about in various directions, taking care, however, to leave the upper side (intended for the channel) and the forepart, to the extent of $\frac{1}{4}$ or $\frac{1}{3}$ of the length of the tube, entirely clean. Fill the tube now nearly with chromate of lead or oxide of copper,—which has previously been cooled in the filling tube or flask,—taking care that the little cylinder which contained the oil be completely filled with the oxidizing agent. Place the tube in hot sand, which, imparting a high degree of fluidity to the oil, leads to the perfect absorption of the latter by the oxidizing agent, and proceed with the combustion in the usual way. It is advisable to select a tolerably long tube. Chromate of lead is usually to be preferred. If it is used, a very intense heat, sufficiently strong to fuse the contents of the tube, is cautiously applied in the last stage of the process.

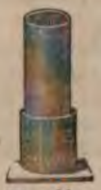

Fig. 89.

Solid fats or waxy substances which, not being reducible to powder, cannot be mixed with the oxidizing agent in the usual way, are treated in a similar manner to fatty oils. They are fused in a small weighed glass boat, made of a tube divided lengthwise; when cold, the little boat with its contents is weighed, and then dropped into the combustion tube, which has been previously filled to the extent of about 6 cm. with chromate of lead, or with oxide of copper. The substance is then fused by the application of heat, and made to spread about in the tube in the same manner as is done with fatty oils; the rest of the operation also being conducted exactly as in the latter case. If chromate of lead is employed, it will be found advantageous to add some bichromate of potassa (§ 177). If oxide of copper be used, finish in a stream of oxygen (§ 176).

2. If it is intended to effect the combustion of fatty substances or other bodies of the kind in a current of oxygen gas, in the apparatus described in § 178, the substance is weighed in a porcelain or platinum boat, which is then inserted into the tube, and the posterior part of the latter filled with oxide of copper, as directed above. The combustion must be conducted with great care. As soon as the oxide of copper in the anterior and the posterior parts of the tube is red-hot, a piece of red-hot charcoal is put to the part occupied by the little boat. The volatile products generated by the dry distillation of the substance burn at the expense of the oxide of copper.

When it is perceived that the surface layer of the oxide of copper is reduced, the application of heat to the substance is suspended for a time, and resumed only after the reduced copper is reoxidized in the stream of oxygen gas. Care is finally taken to insure the complete combustion of the carbon remaining in the boat.

Supplement to A., §§ 174—181.

§ 182.

MODIFIED APPARATUS FOR THE ABSORPTION OF CARBONIC ACID.

G. J. MULDER * has replaced the potash bulbs altogether by a totally different absorption apparatus, viz., by the apparatus already described, p. 293. The chloride of calcium tube is immediately connected with the system of U-tubes, fig. 90; *a* contains small pieces of glass, 6 to 10 drops concentrated sulphuric acid, and at the top asbestos plugs. *b* is filled to $\frac{7}{8}$ with granulated soda-lime (say 20 grm.), the remaining $\frac{1}{8}$ (in the 2d limb) contains chloride of calcium (say 3 grm.). Lastly, *c* is filled with lumps of hydrate of potassa. *a* and *b* are weighed together, *c* serves as a guard to *b*, and is not weighed. The sulphuric acid tube serves to show the rate of the evolution of gas; it contains enough sulphuric acid, when the lower part is just stopped up. If the process goes on properly, the weight of the tube does not increase more than 1 mgrm.; generally the increment is unweighable. If the tube is closed after use with caoutchouc caps, it may be used over and over again. The sulphuric acid possesses the advantage over other fluids that it indicates whether the combustion was complete or not; for in the first case it remains colorless, in the second it becomes brown from the escaping hydrocarbons, and then the results cannot be expected to be perfectly accurate. The absorption of the carbonic acid by the soda-lime tube is as rapid as it is complete;

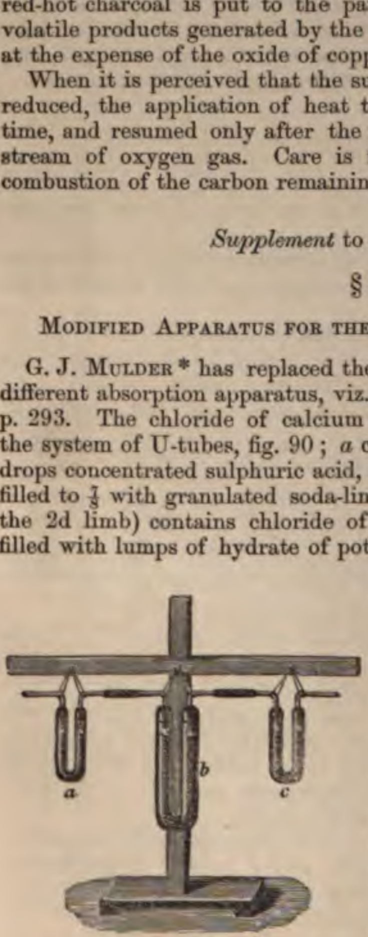

Fig. 90.

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* Zeitschrift f. analyt. Chem. 1, 2.

even when a stream of carbonic acid is passing, with ten times the rapidity usual in organic analysis, no trace of the acid makes its escape. The absorption of the carbonic acid is attended with warming of the soda-lime; if any water evaporates from the soda-lime, it is retained by the chloride of calcium in the second limb. The corks of the absorption tubes are, like the others, coated with sealing-wax. A filled soda-lime tube weighs about 40 grm. The first time it is used alone; the second time the same tube is used, but as a precautionary measure a second similarly filled and separately weighed tube is placed in front of it. The second tube rarely increases in weight, and unless it does, the first tube can be used a third time, but of course in connection with the second. If the second tube has gained in the third operation, the first tube is rejected at the fourth operation, and the second is now used alone, &c. If after the combustion a stream of oxygen is transmitted through the combustion tube, the tubes are of course at the end full of oxygen. If, then, care be taken that the tubes are full of oxygen before weighing, the trouble of the final transmission of air may be saved. For weighing, MULDER closes the ends of the glass tubes with caps made out of india-rubber tube.

MULDER'S absorption apparatus is peculiarly suitable, when the carbonic acid is mixed with another gas. It insures complete absorption, precludes the evaporation of any water, and offers perfect security in case of the sudden occurrence of a too rapid evolution of gas.

B. ANALYSIS OF COMPOUNDS CONSISTING OF CARBON, HYDROGEN, OXYGEN, AND NITROGEN.

The principle of the analysis of such compounds is in general this: in *one portion* the carbon and the hydrogen are determined as carbonic acid and water respectively; in *another portion*, the nitrogen is determined either in the gaseous form, or as chloride of ammonium and bichloride of platinum, or by neutralizing the ammonia formed from the nitrogen; the oxygen is calculated from the loss.

As the presence of nitrogen exercises a certain influence upon the estimation of carbon and hydrogen, we have here to consider not only the method of determining the nitrogen, but also the modifications which the presence of the nitrogen renders necessary in the usual method of determining the carbon and hydrogen.

a. DETERMINATION OF THE CARBON AND HYDROGEN IN NITROGENOUS SUBSTANCES.

§ 183.

1. When nitrogenous substances are ignited with oxide of copper or with chromate of lead, a portion of the nitrogen present escapes in the gaseous form, together with the carbonic acid and aqueous vapor; whilst another portion, minute indeed, still, in bodies abounding in oxygen, not quite insignificant, is converted into nitric oxide gas, which is subsequently transformed wholly or partially into nitrous acid by the air in the apparatus. The application of the methods described in §§ 174, &c., in the analysis of nitrogenous substances would accordingly give too much carbon; since the potash bulbs would retain, besides the carbonic acid, also the nitrous acid formed and a portion of the nitric

oxide (which in the presence of potassa decomposes slowly into nitrous acid and nitrous oxide.) This defect may be remedied by selecting a combustion tube about 12—15 cm. longer than those commonly employed, filling this in the usual way, but finishing with a loose layer, about 9—12 cm. long, of clean, fine copper turnings (§ 66, 5), or a compact roll of copper wire-gauze.* The process is commenced by heating these copper turnings to redness, in which state they are maintained during the whole course of the operation. These are the only modifications required to adapt the methods above described, for the analysis of nitrogenous substances. The use of the metallic copper depends upon its property of decomposing, when in a state of intense ignition, all the oxides of nitrogen into oxygen, with which it combines, and into pure nitrogen gas. As the metal exercises this action only when in a state of intense ignition, care must be taken to maintain the anterior part of the tube in that state throughout the process. As metallic copper recently reduced retains hydrogen gas, and, when kept for some time, aqueous vapor condensed on the surface, the copper turnings intended for the process must be introduced into the tube hot as they come from the drying closet (which is heated to 100°). v. LIEBIG recommends to compress the hot turnings in a tube into a cylindrical form, to facilitate their rapid introduction into the combustion tube.

2. If it is intended to burn nitrogenous bodies in the apparatus described in § 178, the combustion tube should be about 80 cm. long, and the anterior part of it filled with a layer 15 —18 cm. long, of clean copper turnings. Care must be taken to keep at least the anterior half of the turnings from oxidizing, both during the ignition in the current of air and during the actual process of combustion. When the operation is terminated, and the oxidation of the metallic copper is visibly progressing, the oxygen is turned off, and the cock of the air gasometer opened a little instead, to let the tube cool in a slow stream of atmospheric air.

b. DETERMINATION OF THE NITROGEN IN ORGANIC COMPOUNDS.

As already indicated, two essentially different methods are in use for effecting the determination of the nitrogen in organic compounds; viz., the nitrogen is either separated in the pure form and its volume measured, or it is converted into ammonia, and this is determined either as bichloride of platinum and chloride of ammonium, or by neutralization.

α. *Determination of the Nitrogen from the Volume.*

§ 184.

DUMAS' Method, modified by Schiel.

This method may be employed in the analysis of all organic compounds containing nitrogen. It requires a graduated glass cylinder of about 200 c. c. capacity, with a ground-glass plate to cover it.

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* The copper turnings cannot be replaced by the metallic powder obtained by the reduction of the oxide with hydrogen, as this obstinately retains hydrogen, and consequently decomposes appreciable quantities of carbonic acid with formation of carbonic oxide. Schrötter, Lautemann, Journ. f. prakt. Chem. 77, 316.

The combustion tube should be 60 or 70 cm. long, and drawn out at the posterior end to a stout open tail, which should have a small bulb or swell for the better fastening of a rubber tube to it. Introduce into it near the tail a plug of newly ignited asbestos, then a layer of oxide of copper, 4 cm. long; after this the *intimate mixture* of an accurately weighed portion of the substance (0·3—0·6 grm., or, in the case of compounds poor in nitrogen, a somewhat larger quantity) with oxide of copper, then the oxide which has served to rinse the mortar, followed by a layer of pure oxide, and lastly, a layer of copper turnings, about 15 cm. long. Make a channel along the top of the tube by gentle tapping. Connect the tube with the bent delivery tube *c f* (fig. 91), and place in the furnace. Connect the tail by means of a *stout tube* of india rubber with an apparatus for giving a continuous stream of washed carbonic acid gas. Transmit this slowly through the tube for half an hour, then immerse the end of the bent delivery tube under mercury, and invert over it a test tube filled with solution of potassa. If the gas bubbles entering the cylinder are completely absorbed by the solution of potassa, this is a proof that the air is thoroughly expelled from the tube. But should this not be the case, the evolution of carbonic acid must be continued until the desired point is attained. When the gas is completely absorbed, close the communication between the CO_2 generator and the combustion tube by a screw clamp or stop-cock, invert the graduated cylinder, filled $\frac{2}{3}$ with mercury, $\frac{1}{3}$ with concentrated solution of potassa, over the end of the delivery tube, with the aid of a ground-glass plate,* and proceed with the combustion in the usual way, heating first the anterior end of the tube to redness, and advancing gradually towards the farther end. In the last stage of the process, communication is reëstablished with the CO_2 generator, and thus the whole of the nitrogen gas which still remains in the tube is forced into the cylinder. Wait now until the volume of the gas in the cylinder no longer decreases, even upon shaking the latter (consequently, until the whole of the carbonic acid has been absorbed), then place the cylinder in a large and deep glass vessel filled with water, the transport from the mercurial trough to this vessel being effected by keeping the aperture closed with

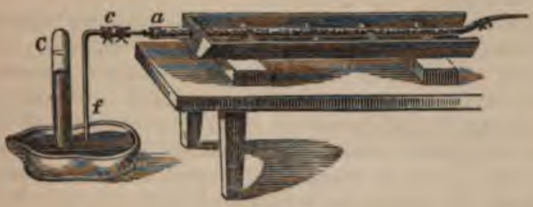

Fig. 91.

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* The following is the best way of filling the cylinder and inverting it over the opening of the bent delivery tube:—The mercury is introduced first, and the air-bubbles which adhere to the walls of the vessel are removed in the usual way. The solution of potassa is then poured in, leaving the top of the cylinder free, to the extent of about 2 lines; this is cautiously filled up to the brim with pure water, and the ground-glass plate slided over it. The cylinder is now inverted, and the opening placed under the mercury in the trough; the glass plate is then withdrawn from under the cylinder. In this manner the operation may be performed easily, and without soiling the fingers.

a small dish filled with mercury. The mercury and the solution of potassa sink to the bottom, and are replaced by water. Immerse the cylinder, then raise it again until the water is inside and outside on an exact level; read off the volume of the gas and mark the temperature of the water and the state of the barometer; calculate the weight of the nitrogen gas from its volume, after reduction to the normal temperature and pressure, and with due regard to the tension of the aqueous vapor (comp. "Calculation of Analyses"). The results are generally somewhat too high, viz., by about 0·2—0·5 per cent.; this is owing to the circumstance that even long-continued transmission of carbonic acid through the tube fails to expel every trace of atmospheric air adhering to the oxide of copper.

It is highly advisable, before making any nitrogen determinations with this method, to subject a non-nitrogenous substance, *e.g.*, sugar, to the same process. The analyst thereby acquaints himself with the extent of the error to which he will be exposed. In such an experiment the quantity of unabsorbed gas should not exceed 1 or 1½ c.c.

To insure complete combustion of difficultly combustible bodies, STRECKER recommends the addition of arsenious acid in powder to the oxide of copper with which the substance is to be mixed; the arsenious acid is volatilized by the action of the heat, the fumes burning the whole of the carbon like a current of oxygen. The arsenious acid sublimes in the anterior part of the tube, arsenic remains in the copper.

[Frankland[*] and Gibbs[†] employ the Sprengel mercury pump to exhaust the combustion tube of air previous to the combustion, and afterwards to transfer the nitrogen to the receiver, and obtain very accurate results.]

β. *Determination of Nitrogen by conversion into Ammonia.*

VARRENTRAPP and WILL's Method.

§ 185.

This method may be applied to all nitrogenous compounds, except those containing the nitrogen in the form of nitric acid, hyponitric acid, &c.[‡] It is based upon the same principle as the method of examining organic bodies for nitrogen (§ 172, 1, *a*), viz., upon the circumstance that, when nitrogenous bodies are ignited with the hydrate of an alkali, the water of hydration of the latter is decomposed, the oxygen forming with the carbon of the organic body carbonic acid, which then combines with the alkali, whilst the hydrogen at the moment of its liberation combines with the whole of the nitrogen present to ammonia.

In the case of substances abounding in nitrogen, such as uric acid, mellon, &c., the whole of the nitrogen is not at once converted into ammonia in this process; a portion of it combining with part of the carbon of the organic matter to cyanogen, which then combines, either in that form with the alkali metal, or in form of cyanic acid with the alkali. Direct experiments have proved, however, that even in such cases the whole of the nitrogen is ultimately obtained as ammonia, if the hydrated alkali is present in excess, and the heat applied sufficiently intense.

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[*] [Journal Chem. Soc., 1868, p. 90.]

[†] [Unpublished paper read before National Academy of Sciences, Aug., 1868.]

[‡] [Vegetable matters, as dried plants, containing not more than 3 per cent. of NO_5 may be analyzed by this method. In a case where 6 per cent. of NO_5 was present, a loss of 0·2 per cent. of N took place in the experiments of E. Schulze.—Fres. Zeitschrift vi., 387].

As in all organic nitrogenous compounds the carbon preponderates over the nitrogen, the oxidation of the former, at the expense of the water, will invariably liberate a quantity of hydrogen more than sufficient to convert the whole of the nitrogen present into ammonia; for instance,

$$C_2N+4\ H\ O=2\ C\ O_2+N\ H_3+H.$$

The excess of the liberated hydrogen escapes either in the free state, or in combination with the not yet oxidized carbon, according to the relative proportions of the two elements and the temperature, as marsh gas, olefiant gas, or vapor of readily condensible hydrocarbons, which gases serve in a certain measure to dilute the ammonia. As a certain dilution of that product is necessary for the success of the operation, I will here at once state that substances rich in nitrogen should be mixed with more or less of some non-nitrogenous body— sugar, for instance— so that there may be no deficiency of diluent gas.

The ammonia is determined volumetrically, see § 208.

aa. Requisites.

1. The objects enumerated § 174, and a **Porcelain Mortar** for weighing and mixing the substance.

2. A **Combustion-tube** of the kind described § 174, 3; length about 40 cm., width about 12 mm. The combustion is effected in an ordinary combustion furnace (§ 174, 11).

3. **Soda-Lime.**—(§ 66, 4). It is advisable to gently heat in a platinum or porcelain dish, a quantity of the soda-lime sufficient to fill the combustion tube, so as to have it perfectly dry for the process of combustion. In the analysis of non-volatile substances, the best way is to use the soda-lime while still warm.

4. **Asbestos.**—A small portion of this substance is ignited in a platinum crucible previous to use.

5. A **Varrentrapp and Will's Bulb-apparatus.**—This may be obtained from the shops. Fig. 92 shows its form. It is filled to the extent indicated in the drawing with standard sulphuric acid § 204, of which 20 c.c. should be employed. The acid is introduced either by dipping the point into the acid, and applying suction to *d*, or by means of a burette.

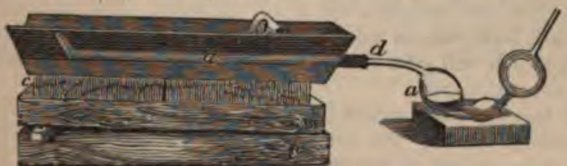

Fig. 92.

In order to guard against the receding of the acid into the combustion tube, **Arendt** and **Knop** have suggested the form indicated fig. 93.

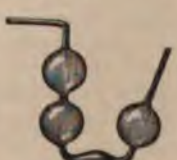

Fig. 93.

6. A soft, well-perforated **Cork**, which fits the combustion tube air-tight, and in which the tube *d* of the bulb apparatus fits closely.

7. A **Suction-tube** of caoutchouc adapted to the point of the bulb apparatus.

bb. The Process.

The combustion tube is half filled with soda-lime, which is then gradually transferred to the perfectly dry, and, if the nature of the substance permits, rather warm mortar, where it is most intimately mixed with the weighed substance, forcible pressure being carefully avoided; a layer of soda-lime, occupying about 3 cm., is now introduced into the posterior part of the combustion tube, and the mixture filled-in after; the latter, which will occupy about 20 cm., is followed by a layer of about 5 cm. of soda-lime, which has been used to rinse the mortar, and this again by a layer of 12 cm. of pure soda-lime, leaving thus about 4 cm. of the tube clear. The tube is then closed with a loose plug of asbestos, and a free passage for the evolved gases formed by a few gentle taps; it is then connected with the bulb apparatus by means of the perforated cork, and finally placed in the combustion furnace (see fig. 92).

To ascertain whether the apparatus closes air-tight, some air is expelled by holding a piece of red-hot charcoal to the bulb *a*, and the apparatus observed, to see whether the liquid will, upon cooling, permanently assume a higher position in *a* than in the other limb. The tube is then gradually surrounded with ignited charcoal, commencing at the anterior part, and progressing slowly towards the tail, the operation being conducted exactly as in an ordinary combustion (§ 175). Care must be taken to keep the anterior part of the tube tolerably hot throughout the process, since this will almost entirely prevent the passage of liquid hydrocarbons, the presence of which in the standard acid would be inconvenient. The asbestos should be kept sufficiently hot to guard against its retaining water, and with this, ammonia. The combustion should be conducted so as to maintain a steady and uninterruped evolution of gas; there is no fear of any ammonia escaping unabsorbed, even if the evolution is rather brisk; but the operator must constantly be on his guard against the receding of the acid, which takes place the moment the evolution of gas ceases, and this, in some instances, with such impetuosity as to force the acid into the combustion tube, which of course spoils the whole analysis. This difficulty may be readily met, however, by mixing with the substance an equal quantity of sugar, which will give rise to the evolution of more permanent gases diluting the ammonia.

When the tube is ignited in its whole length, and the evolution of gas has *totally* ceased,* the point of the combustion tube is broken off, and air to the extent of several times the volume of the gas in the tube is sucked through the apparatus, to force all the rest of the ammonia into the acid.

Liquid nitrogenous compounds are weighed in small sealed glass bulbs, and the process is conducted as directed § 180, with this difference, that soda-lime is substituted for oxide of copper. It is advisable to employ tubes of greater length for the combustion of liquids than are required for solid bodies. The best method of conducting the operation, is to heat first about one-third of the tube at the anterior end, and then to force the liquid from the bulbs into the tube by heating the hinder end of the latter; the expelled liquid will thus become diffused in the central part of the tube, without being decomposed. By a progressive application of heat, proceeding slowly from the anterior to the posterior end, a steady and uniform evolution of gas may be easily maintained.

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* This is indicated by the white color which the mixture reassumes when all the carbon deposited on the surface is oxidized.

When the combustion is terminated, the bulb apparatus is emptied, through the opening at the point into a beaker, and rinsed with water until the rinsings cease to manifest acid reaction.

The excess of acid is determined by means of standard potash solution and cochineal tincture, or, if the acid is so colored that the point of neutralization cannot readily be decided by cochineal, employ slips of turmeric paper (see § 208).

It is advantageous to use a rather dilute acid, 1 c.c.=0·005 grm. of nitrogen. The receiver (fig. 94) may be advantageously substituted for the bulb-tube. The tube *a*—previously provided with the caoutchouc stopper *b*—is first connected by the aid of a good cork with the combustion tube, and then the U-tube *c*—having been charged with the proper quantity of acid from a MOHR's burette—is added. At the termination of the combustion, when air has been drawn through the apparatus, the tube *a* is rinsed into the apparatus *c*, some tincture of cochineal added, and standard alkali run into the tube from a second burette, until the acid is almost neutralized. Now pour the contents of the apparatus into a beaker, rinse with water, and complete the neutralization. With this receiver neither receding nor spirting is possible. By not pouring out the fluid till the point of saturation is nearly attained, you require less water for rinsing the tube. This method is rapid and accurate.

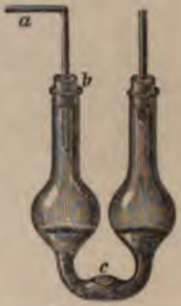

Fig. 94.

[Iron gas tubes may be advantageously substituted for glass tubes. They are closed at the rear with a cork, carrying a bit of glass tube drawn out to a sealed tail. The mixture is confined to its place by loose asbestos plugs. The corks are kept from charring by wrapping the end of the tube with two or three thicknesses of filter-paper, which is kept wet by a wash-flask, or by dipping the depending end into a vessel of water. The tubes should be 45 cm. long, and 5 cm. at each end should project from the fire and be protected with wet paper.

C. ANALYSIS OF ORGANIC COMPOUNDS CONTAINING SULPHUR.*

§ 186.

The usual method of determining the carbon in organic bodies—viz., by combustion with oxide of copper or chromate of lead—would give results too high in the analysis of compounds containing sulphur, since—more especially if oxide of copper is used—a portion of the sulphur would be converted in the process into sulphurous acid, which would be absorbed with the carbonic acid in the potash bulbs. CARIUS recommends to burn substances containing sulphur in a tube 60—80 cm. long, with chromate of lead, care being taken that the anterior 10—20 cm., which contain pure chromate of lead, are never heated above low redness. The chromate of lead may be used again three or four times without refusion; and, finally, if treated by VOHL's method (p. 97), it

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[* Warren's method of determining carbon, hydrogen, and sulphur in one operation is described in Am. Jour. Sci., vol. 41, 2d ser., p. 40.]

is just as fit for use as if it had not been employed for the combustion of a substance containing sulphur.

The presence of sulphur demands no modification in the process described §§ 184 and 185, for the determination of nitrogen. In substances containing oxygen in presence of sulphur, the oxygen is estimated from the loss.

As regards the *estimation of the sulphur* in organic compounds, that element is invariably weighed in the form of sulphate of baryta, into which it may be converted either in the dry or in the wet way.

a. Methods in the Dry Way.

1. *Method suitable, more particularly, to determine the sulphur in non-volatile Substances poor in Sulphur, e.g., in the so-called Protein Compounds* (v. LIEBIG).

Put some lumps of hydrate of potassa, free from sulphuric acid (§ 66, 6. c), into a capacious silver dish, add ⅛ of pure nitrate of potassa, and fuse the mixture, with addition of a few drops of water. When the mass is cold, add to it a weighed quantity of the finely pulverized substance, fuse over the lamp, stir with a silver spatula, and increase the heat, continuing the operation until the color of the mass shows that the carbon separated at first has been completely consumed. Should this occupy too much time, you may accelerate it by the addition of nitrate of potassa in small portions. Let the mass cool, then dissolve in water, supersaturate the solution with hydrochloric acid in a capacious beaker covered with a glass dish, and precipitate with chloride of barium. Wash the precipitate well with boiling water, first by decantation, then on the filter. Dry and ignite. Treat the ignited sulphate of baryta as directed p. 265; if this latter operation is omitted, the result is almost always too high.

2. *Method adapted more particularly for the Analysis of non-volatile or difficultly volatile Substances containing more than 5 per cent. of Sulphur* (KOLBE*).

Introduce into the posterior part of a straight combustion tube,† 40—45 cm. long, a layer, 7—8 cm. long, of an intimate mixture of 8 parts of pure anhydrous carbonate of soda, and 1 part of pure chlorate of potassa; after this introduce the weighed substance, then another layer, 7 or 8 cm. long, of the same mixture; mix the organic compound intimately with the carbonate of soda and chlorate of potassa, by means of the mixing wire (fig. 76, p. 426); fill up the still vacant part of the tube with anhydrous carbonate of soda or potassa mixed with a little chlorate of potassa. Clear a *wide* passage from end to end by a few gentle taps, place the tube in a combustion furnace, heat the anterior part to redness, and then, progressing slowly toward the posterior part, proceed to surround with red-hot charcoal the part occupied by the mixture. In the analysis of substances abounding in carbon, it is advisable to introduce into the posterior part of the tube a few lumps of pure chlorate of potassa, to insure complete combustion of the carbon, and perfect conversion into sulphates of the compounds of potassa with the lower oxides of sulphur that may have formed. The sulphuric acid in the contents of the tube is determined as in 1.

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[*] Supplemente zum Handwörterbuch. 205.

[†] Sealed and rounded at the end like a test tube.

3. *Method adapted for the Analysis both of non-volatile and volatile Substances, but more especially the latter* (DEBUS*).

Dissolve 1·eq. (149 parts) of bichromate of potassa purified by recrystallization, and 2 eq. of carbonate of soda (106 parts) in water, evaporate the solution to dryness, reduce the lemon-colored saline mass ($KO, CrO_3 + NaO, CrO_3 + NaO, CO_2$) to powder, heat to intense redness in a Hessian crucible, and transfer still hot to a filling-tube (fig. 75, p. 426).† When the powder is cold, introduce a layer of it, 7—10 cm. long, into a common combustion tube; then introduce the substance, and after this another layer, 7—10 cm. long, of the powder. Mix intimately by means of the mixing wire, then fill the still unoccupied part of the tube with the saline mixture, and apply heat as in an ordinary ultimate analysis. When the entire mass is heated to redness, conduct a slow stream of dry oxygen gas over it for ½—1 hour. When cold, wipe the ash off the tube, cut the latter into several pieces over a sheet of paper, and treat them in a beaker with a sufficient quantity of water to dissolve the saline mass. Add hydrochloric acid in tolerable excess, then some alcohol, and apply a gentle heat until the solution shows a beautiful green color; filter off the sesquioxide of chromium produced by the combustion (this contains sulphuric acid); wash first with water containing hydrochloric acid, then with alcohol, dry, and transfer to a platinum crucible; add the filter-ash, mix with 1 part of chlorate and 2 parts of carbonate of potassa (or soda), and ignite until the sesquioxide of chromium is completely converted into alkaline chromate. Dissolve the fused mass in dilute hydrochloric acid, and reduce by heating with alcohol; add the solution to the fluid filtered from the sesquioxide of chromium, heat the mixture to boiling, and precipitate the sulphuric acid with chloride of barium. DEBUS's test-analyses were very satisfactory; thus he obtained 99·76 and 99·50 of sulphur for 100, again 30·2 of sulphur in xanthogenamide for 30·4, &c.

4. *Method equally adapted for the Analysis of Solid and Liquid Volatile Compounds.* (W. J. RUSSELL;‡ suggested by BUNSEN.)

Introduce into a combustion tube, 40 cm. long, sealed at the posterior end, first 2—3 grm. pure oxide of mercury, then a mixture of equal parts of oxide of mercury and pure anhydrous carbonate of soda, mixed with the substance, and fill up the tube with carbonate of soda mixed with a little oxide of mercury. Connect the open end of the tube with a gas delivery tube dipping under water, to effect the condensation of the mercurial fumes. Place a screen in front of the part of the tube occupied by the substance, then heat the anterior part to bright redness, and maintain this temperature during the entire process. At the same time, heat another portion of the tube, nearer to the end, but not to the same degree of intensity, so that there may be alternate parts in the tube in which the oxide of mercury is left undecomposed. When the part before the screen is at bright redness, remove the screen, heat the mixture containing the substance, regulating the application of heat so as to insure complete decomposition in the course of 10—15 minutes, and heat at the same time the still unheated parts of the tube, and lastly also the pure oxide of mercury at the extreme end. The gas must be tested from time to time, to ascertain whether it contains free oxygen. Dissolve the contents of the tube in water, add some chloride of mercury, to decompose the sulphide of sodium which may have formed, acidify the hydrochloric acid, oxidize the sulphide of mercury which may have formed with chlorate of potassa, and finally precipitate the sulphuric acid with chloride of barium. W. J. RUSSELL obtained by this method very satifactory results in the analysis of pure sulphur, sulphocyanide of potassium, and bisulphide of carbon.

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* Annal. d. Chem. u. Pharm. 76, 90.

† The saline mass must always first be tested for sulphur. For this purpose a small portion of it is reduced with hydrochloric acid and alcohol, chloride of barium added, and the mixture allowed to stand 12 hours at rest. No trace of a precipitate should be discernible.

‡ Quart. Journ. Chem. Soc. 7, 212.

*b. Method in the Wet Way.**

According to RIVOT, BEUDANT, and DAGUIN,† the sulphur in organic compounds may be readily determined by heating with pure solution of potassa, adding 2 volumes of water and conducting chlorine into the fluid. When the oxidation is effected, the solution is acidified and freed from the excess of chlorine by application of heat, then filtered, and the filtrate precipitated by chloride of barium. Mr. C. J. MERZ, in my laboratory, has employed both this method and v. LIEBIG'S (*a*, 1) in the analysis of fine horn shavings. The process appears convenient and exact.‡

Substances leaving an ash on incineration, and which may therefore be presumed to contain sulphates, are boiled with hydrochloric acid; the solution obtained is filtered, and the filtrate tested with chloride of barium. If a precipitate of sulphate of baryta forms, the sulphur contained in it is deducted from the quantity found by one of the methods described above; the difference gives the quantity of the sulphur which the analyzed substance contains in organic combination.

D. DETERMINATION OF PHOSPHORUS IN ORGANIC COMPOUNDS.

§ 187.

MULDER, who has occupied himself much with the determination of phosphorus in organic substances, recommends the following method :—

Dissolve a weighed portion of the substance by boiling with hydrochloric acid; filter, if necessary, and determine the phosphoric acid which the fluid may contain, by BERTHIER'S method (§ 134, I., *d*). Boil another weighed portion of the substance with nitric acid, and treat the fluid in the same way as the hydrochloric acid solution. If you find in both cases the same percentage of phosphoric acid, the substance contains the phosphorus only in the form of phosphoric acid; but if you obtain a larger proportion of acid in the second experiment than in the first, the difference indicates the quantity of phosphoric acid formed by the action of the nitric acid upon

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[* For the excellent processes of Carius, see Annal. d. Chem u. Pharm. 116, 11.]

† Comp. rend. 37, 835; Journ. f. prakt. Chem. 61, 135.

‡ Two experiments were made with each method, on horn dried at 100°. The percentages obtained were as follows:—By v. Liebig's method, 3·37 and 3·345; by the present method, 3·31 and 3·33.

phosphorus contained in the analyzed compound in the unoxidized state.

The phosphorus cannot be determined by incineration of the substance and examination of the ash. Vitellin, which, when treated with nitric acid, gives 3 per cent. of phosphoric acid, yields barely 0·3 per cent. of ash (v. BAUMHAUER).

The methods described in § 186, *a*, 1, 2, 4, and *b*, may also be employed to determine the total quantity of phosphorus in organic substances.

E. ANALYSIS OF ORGANIC SUBSTANCES CONTAINING CHLORINE, BROMINE, OR IODINE.

§ 188.

Substances containing Bromine and Iodine are analyzed generally in the same manner as those containing Chlorine.

Those portions of the following § which are enclosed between square brackets refer exclusively to combinations of Iodine or Bromine, as the case may be.

The combustion of organic substances containing chlorine with oxide of copper gives rise to the formation of subchloride of copper, which, were the process conducted in the usual manner, would condense in the chloride of calcium tube, and would thus vitiate the determination of the hydrogen. This and every other error may be prevented by the employment of chromate of lead (§ 177). The chlorine is, in that case, converted into chloride of lead, and retained in that form in the combustion tube.

If the combustion is effected with oxide of copper in a current of oxygen, the subchloride of copper is decomposed by the oxygen, oxide of copper and free chlorine being formed; the latter is retained partly in the chloride of calcium tube, partly in the potash bulbs. To remedy this defect, STAEDELER * proposes to fill the anterior part of the tube with clean copper turnings; these must be kept red-hot during the combustion, and the current of oxygen must be arrested the moment they begin to oxidize. K. KRAUT † observes with reference to this process that it is well to place a roll of silver foil, about 5 inches long, in front of the layer of metallic copper. In the absence of the silver the transmission of oxygen has to be conducted with caution, in order that no chlorine may be expelled from the subchloride of copper first formed, but by adopting KRAUT's recommendation we may continue passing the gas without fear till it escapes free from the potash tube. [In the case of substances containing iodine, it is needless to employ metallic copper as well as silver foil.] The silver may be used over and over again, but at last requires ignition in a stream of hydrogen. According to A. VÖLCKER,‡ the evolution of chlorine may be prevented by mixing the oxide of copper with $\frac{1}{5}$ oxide of lead.

[In the analysis of bodies containing bromine the above methods do not always answer. v. GORUP-BESANEZ ‖ satisfied himself of this by analyzing dibromotyrosin. Whether this body was burnt with chromate of lead, with a mixture of chromate of lead and chromate of potash, with oxide of copper and oxygen and an anterior layer of chromate of lead, with an anterior layer of copper turnings, whether mixed or in the platinum boat, in whichever way the analysis was performed the carbonic acid always came out several per-cents too low, because metallic bromide was formed, which fused and enclosed carbon, thereby preventing its oxidation. The following process, on the contrary, yielded good results:—Into a combustion tube drawn out to a long point, introduce first a three-inch layer of oxide of copper, then a plug of asbestos, then a mixture of the substance (finely powdered) with about an equal weight of well-dried oxide of lead in a porcelain boat; again a plug of asbestos, then granulated oxide of copper, then chromate of lead or copper turnings. First heat the anterior and then the posterior layers to ignition, and warm the part, where the boat is, very cautiously and gradually: everything combustible distils over, arrives at the oxide of copper in the form of vapor, and is there burnt. In the boat nothing remains but a mixture of bromide and oxide of lead. Complete the combustion with oxygen, taking care not to heat the point where the boat is too strongly, nor continue the transmission of oxygen longer than necessary. Observe also that no bromide of copper sublimes into the chloride of calcium tube.]

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* Annal. d. Chem. u. Pharm. 69, 335.

† Zeitschrift f. analyt. Chem. 2, 242.

‡ Chem. Gaz. 1849, 245. 29.

‖ Zeitschrift f. analyt. Chem. 1, 439.

As regards the determination of the *chlorine itself*, this is usually effected either (*a*) by igniting the substance with alkalies or alkaline earths, by which process all the chlorine is obtained as chloride, or (*b*) by oxidizing the substance with nitric acid, &c., in a sealed tube.

a. As chlorine-free lime is easily obtainable (by burning marble), this body is usually preferred to effect the decomposition. It must always be tested for chlorine previous to use.

Introduce into a combustion tube, about 40 cm. long, the posterior end of which is sealed and rounded like a test tube, a layer of lime, 6 cm. long, then the substance, after this another layer of lime, 6 cm. long, and mix with the wire; fill the tube almost to the mouth with lime, clear a free passage for the evolved gases by a few gentle taps, and apply heat in the usual way. Volatile fluids are introduced into the tube in small glass bulbs. When the decomposition is terminated, dissolve in dilute nitric acid, and precipitate with solution of nitrate of silver (§ 141). KOLBE recommends the following process to obtain the contents of the combustion tube:—When the decomposition is completed, remove the charcoal, insert a cork into the open end of the tube, remove every particle of ash, and immerse the tube, still hot, with the sealed end downwards, into a beaker filled two-thirds with distilled water; the tube breaks into many pieces, and the contents are then more readily acted upon. As in this method the ignition of compounds abounding in nitrogen may be attended with formation of cyanide of calcium or cyanide of sodium, the separation of the chloride and the cyanide of silver, if required, is to be effected by the process given in § 169, 6 (NEUBAUER and KERNER[*]). In the analysis of acid organic compounds containing chlorine (e.g., chlorosalicylic acid), the chlorine may often be determined in a simpler manner, viz., by dissolving the substance under examination in an excess of dilute solution of potassa, evaporating to dryness, and igniting the residue, by which means the whole of the chlorine present is converted into a soluble chloride (LIEBIG).

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[*] Annal. d. Chem. u. Pharm. 101, 324, 344.

b. In more readily decomposable compounds, *e. g.*, in the substitution products of acids, the halogen may also be determined by decomposing the substance by contact during several hours with water and sodium amalgam, acidifying the fluid with nitric acid, and precipitating with silver solution (KEKULÉ *).

F. ANALYSIS OF ORGANIC COMPOUNDS CONTAINING INORGANIC BODIES.

§ 189.

In the analysis of organic compounds containing inorganic bodies, it is, of course, necessary first to ascertain the quantity of the latter before proceeding to the determination of the carbon, &c., as otherwise the amount of the organic body whose constituents have furnished the carbonic acid, water, &c., not being known, it would be impossible to estimate the oxygen from the loss.

If the substances in question are salts or similar compounds, their bases are determined by the methods given in the Fourth Section; but in cases where the inorganic bodies are of a nature to be regarded more or less as impurities (*e.g.*, the ash in coal), they may usually be determined with sufficient accuracy by the combustion of a weighed portion of the substance in an obliquely placed platinum crucible, or in a platinum dish. In the analysis of substances containing fusible salts, even long-continued ignition will often fail to effect complete combustion, as the carbon is protected by the fused salt from the action of the oxygen. In such cases, the best way to effect the purpose is to carbonize the substance, treat the mass with water, and incinerate the undissolved residue; the aqueous solution is, of course, likewise evaporated to dryness, and the weight of the residue added to that of the ash.

If organic compounds whose ash contains potassa, soda, baryta, lime, or strontia, are burnt with oxide of copper, part of the carbonic acid evolved remains combined with the bases. As, in many cases, the amount of carbonic acid thus retained is not constant, and the results are, moreover, more accurate if the whole amount of the carbon is expelled and weighed as carbonic acid, the combustion is effected with chromate of lead, with addition of $\frac{1}{8}$ of bichromate of potassa, according to the directions given in § 177. Accurate experiments have shown that in this case not a trace of carbonic acid remains with the bases.

If the substance is weighed in a porcelain or platinum boat, and the combustion is effected according to § 178, the ash, carbon, and hydrogen may be determined in one portion. The amount of carbonic acid contained in the ash is added to that found by the process of combustion; if the carbonic acid in the ash cannot be calculated, as in the case of carbonates of the alkalies, it may be determined by means of fused borax (§ 139, II., *c*).

In burning substances containing mercury, the arrival of any of the metal at the chloride of calcium tube may be prevented by having a layer of copper-turnings in the anterior part of the combustion tube, and by not allowing the foremost portion to get too hot.

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* Jahresb. v. Kopp. u. Will. 1861, 832.

III. DETERMINATION OF THE EQUIVALENT OF ORGANIC COMPOUNDS.

The methods of determining the equivalent of organic compounds differ essentially according to the properties of the various compounds. There are three general methods in use for this purpose, which I will proceed to describe.

§ 190.

1. *We ascertain the amount of a Body of known Equivalent, which forms a well-characterized Compound with the Substance whose Equivalent is to be determined.*

This method is pursued in determining the equivalent of the organic acids and organic bases, and of many indifferent bodies possessed of the property of combining with bases or acids. We occupy ourselves here simply with the process; the mode of calculating the equivalent from the results obtained will be found under "The Calculation of Analyses."

a. The equivalent of *organic acids* is, in most cases, determined from the silver salt, because the analysis of this is very simple, and there is almost always the positive certainty that the analyzed salt is not a basic or hydrated compound. Other salts also are, however, frequently used for the same purpose, particularly those of lead, baryta, and lime. (In the analysis of the lead salts, especial care must be taken not to mistake basic for neutral, nor in the analysis of the baryta and lime salts, hydrated for anhydrous salts.) For the manner in which the determination of the bases in question is effected, I refer to Section IV.

b. The equivalent of *organic bases* forming well-crystallizable salts with sulphuric, hydrochloric, or any other easily determined acid, is best ascertained by estimating, by the usual methods, the acid contained in a weighed amount of the salt.

If the salts do not crystallize, a known quantity of the dry alkaloid is (after v. LIEBIG) introduced into a drying tube (fig. 95), which is then accurately weighed with its contents; a slow current of dry hydrochloric acid gas is transmitted through the apparatus for some time; the tube ultimately heated to 100° (see p. 38, fig. 21), and a stream of atmospheric air transmitted through it; the quantity of the hydrochloric acid absorbed is found from the increase in the weight of the tube. The accuracy of the results may be controlled by dissolving the hydrochlorate in water, and precipitating the chlorine from the solution by nitrate of silver. The equivalent of the alkaloids may be determined also from the insoluble double salts produced by precipitating the solution of their hydrochlorates with bichloride of platinum; the double chlorides thus produced are cautiously ignited (§ 124), and the residuary platinum weighed.

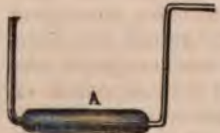

Fig. 95.

c. In the case of *indifferent bodies*, there is usually no choice about the matter, and we have to determine the equivalent from the lead compound; since many of these substances either altogether refuse to enter into combination with other bases besides lead, or only form with them compounds which cannot be obtained in a state of purity. Although the determination of the equivalent of an indifferent body from the compound which the latter forms with lead is liable to leave the matter in doubt, as the oxide of lead will often combine with such substances in varying proportions, yet the analysis of such compounds is always interesting in this—that we learn by it whether the organic body combines with the oxide of lead without alteration, or gives up water upon entering into combination.

Organic substances will also occasionally form with water solid and crystallizable compounds, by the analysis of which the equivalent of the organic body may be determined.

§ 191.

2. *The Specific Gravity of the Vapor of the Compound is determined.*

Of the numerous methods which have been proposed for the accomplishment of this object, I shall describe only those two which are more frequently employed in laboratories as the simplest and most suitable. In all determinations of vapor densities it is necessary that the temperature at which they are made should be sufficiently raised (at least 30—40° above the boiling point of the substances), so that the vapor may possess the coefficient of expansion of the gases. The extreme importance of this rule is evident from the fact that at temperatures only slightly above the boiling point higher densities are found, the densities decreasing with the increase of temperature, and becoming constant only after a certain point.

A. Process of Dumas.

The following are the outlines of this method:—A light glass globe, filled with dry air, and the exact capacity of which is afterwards ascertained, is accurately weighed; the weight of the air in the globe is calculated at the temperature and atmospheric pressure observed during the process of weighing, and the result subtracted from the first weight: the difference expresses the weight of the exhausted vessel. A more than sufficient quantity of the substance, the density of the vapor of which it is intended to determine, is then introduced into the globe, and exposed to a uniform temperature sufficiently above the boiling point of the substance, until the latter is completely converted into vapor, and the excess expelled, together with the atmospheric air originally contained in the globe; the vessel is then sealed air-tight, and weighed. The difference between the weight found and that of the exhausted globe, expresses the weight of a given volume of the vapor; supplying thus the necessary data for calculating its specific gravity.

It is hardly necessary to remark that the volume of the air and the vapor must be reduced to the same pressure and temperature, and consequently that the state of the barometer and thermometer must be noted both during the first weighing and at the time of sealing the glass globe.

This method is of course applicable only to substances which volatilize without suffering decomposition. To obtain accurate results, it is indispensable that the substance be perfectly pure.

I will now proceed to describe the process; for the manner of correcting and calculating the results, and inferring from them the composition of the bodies examined, I refer to § 204.

a. Apparatus and other Requisites.

1. The Substance.—From 6 to 8 grammes are required. The boiling point must be pretty accurately known.

2. A light Glass Globe with drawn-out Neck.

An ordinary globe of pure glass is selected, free from flaws and holding from 250 to 500 c. c.; it is carefully rinsed with water, and then thoroughly dried. After this, it is completely exhausted, dry air readmitted into it, and the same operation repeated. The neck of the globe is then softened near the bulb, and drawn out in the shape represented in fig. 96.

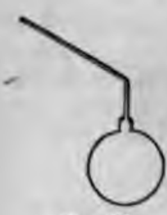

Fig. 96.

The extreme point is cut off, and the edges slightly rounded over the spirit-lamp. (This point having to be sealed air-tight with the greatest despatch, at a subsequent stage of the process, it is advisable to ascertain, in the first place, whether the glass of the globe is readily fusible or not; this may be done by trying to seal the point on the original neck of the balloon; should this present any difficulty, the globe is unfit for the intended purpose.)

3. A small Iron or Copper Vessel for the reception of the fluid in which the globe is to be heated (see fig. 97). The fluid which is to serve as bath must admit of being heated to at least 30—40° beyond the boiling point of the substance under examination. Oil will answer the purpose in nearly all cases where a temperature higher than that of boiling water is required; however, a chloride of calcium bath—if its temperature, which in a perfectly saturated bath may be raised to 180°, is sufficiently high for the purpose—is more convenient than an oil-bath, as the globe may be more easily cleaned.

4. An Apparatus to keep the Globe in Position.—This may be readily made with a handle and some iron wire. During the operation, it is attached to a retort-stand (see fig. 97).

5. A quantity of Mercury more than sufficient to fill the globe.

6. A graduated Tube of about 100 c. c. capacity.

7. A Gas- or Spirit-lamp and Blowpipe.

8. A correct Barometer.

9. A correct Thermometer, capable of indicating the highest degree of heat the case under examination may require.

b. The Process.

α. Weigh the globe, placing a thermometer inside the case of the balance. Leave the globe for ten minutes on the scale, to ascertain whether its weight remains constant. If so, the weight is noted, together with the height of the barometer, and the temperature indicated by the thermometer inside the case.

β. Heat the globe gently, and dip the point deep into about 8 grm. of the substance, which, if solid, must have been liquefied by the application of a gentle heat. (If the substance under examination has a high fusing point, the neck and point of the globe likewise require heating, to guard against the fluid solidifying too soon.) When the globe has cooled—which, in the case of very volatile substances, is to be accelerated by dropping ether upon it—the fluid enters and spreads in it. Do not introduce more than 5—7 grm.

γ. Heat the contents of the vessel 3 to from 40 to 50°, and immerse the globe by means of the apparatus 4, and also a thermometer, in the bath, as shown in fig. 97.

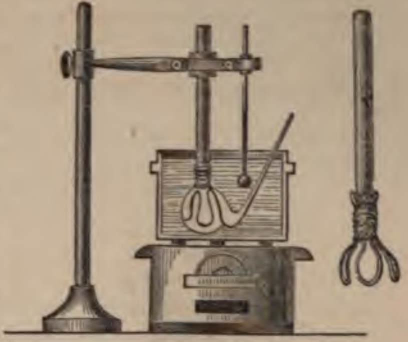
Fig. 97.

Raise the temperature of the bath to between 30 and 40° above the boiling point of the substance.* As soon as the temperature in the globe is somewhat higher than the boiling point of the substance, the vapor of the latter rushes out through the orifice of the neck; the force of the current increases at first with the temperature of the bath, but diminishes afterwards by degrees, and finally (after about 15 minutes) ceases altogether. Should any of the vapor have condensed into drops in the point of the neck projecting out of the bath, these may be at once reconverted into vapor, by moving a piece of red-hot charcoal to and fro under it. The moment that a perfect equilibrium is fully established at the desired temperature, seal the point of the globe, by means of a spirit-lamp and blowpipe, and note immediately after the height of the thermometer. To ascertain whether or not the point is hermetically sealed, you need simply direct a current of air through the blowpipe upon the projecting point of the neck: if the tube is closed hermetically, a small portion of the vapor condenses, forming a column of fluid, which is retained in the end of the tube by capillary attraction; this is not observed if the tube is not hermetically sealed. The height of the barometer also is noted again, if it has changed since the first observation.

δ. Remove the sealed globe from the bath, allow to cool, wash most carefully, wipe perfectly dry, and weigh again in the same manner as before.

ε. Immerse the pointed end of the globe in its entire length in mercury, scratch a mark with a file near the end, and break off the point; whereupon the mercury will immediately rush into the globe, a vacuum having been created in it by the condensation of the vapor. (In this operation, place the glass globe in the hollow of your hand, and rest the latter upon the edge of the mercurial trough.) If the globe, at the moment of sealing, was perfectly free from air, it will fill completely with mercury; otherwise, an air-bubble will remain in it. In either case transfer the mercury from the globe to the graduated tube (6), and measure accurately; if there was air in the globe at the moment of sealing it, fill it now with water, and measure also the volume of the latter liquid: the difference between the volume of the mercury and that of the water shows the volume of the air which had remained in the globe.

This method, if properly executed, gives nearly accurate results; for the manner of calculating the latter, I refer to § 201.

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* If a chloride of calcium or oil-bath is used, you must endeavor to maintain a uniform temperature towards the end of the process, which may be easily effected by properly regulating the heat.

B. Process of Gay-Lussac.

Whilst by the method of **Dumas** the weight of the amount of substance is determined, which yields under definite circumstances a known volume of vapor, by **Gay-Lussac**'s method is determined the volume of vapor yielded under definite circumstances by a previously weighed amount of substance. The original process has been judiciously modified by H. **Schiff**.* The apparatus is excessively simple, but can only be employed for temperatures under 200°,—it is especially suited for temperatures under 100°.

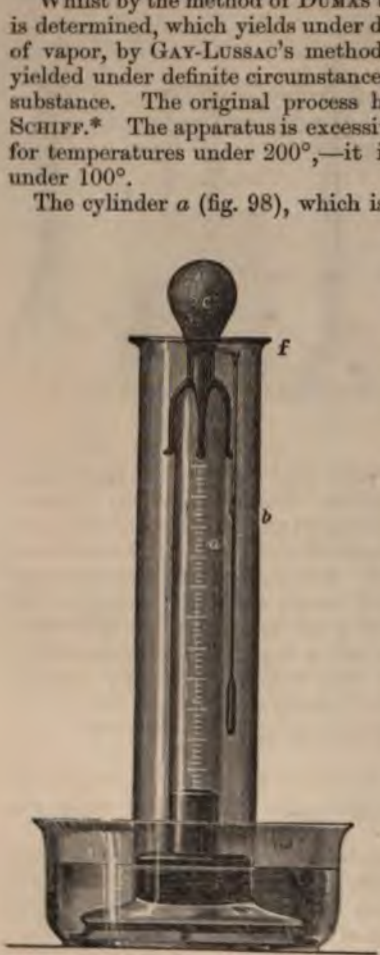

Fig. 98.

The cylinder *a* (fig. 98), which is destined to measure the volume of the vapor, is 30—35 cm. high and about 2 cm. wide; it is provided with a millimetre scale, extending to the open end; a table which must previously be drawn up, shows the c. c. corresponding to the marks (p. 19). The outer cylinder *b* is about 40 cm. high, and broad in proportion. The height of the latter in the inside must be accurately known in mm. The handle *c*, which is filled with lead, embraces the closed end of the measuring tube by means of four springs. The weight of this handle must suffice to depress the tube when filled with vapor, and must therefore be about 130 grm., if the above dimensions are strictly adhered to. The handle bears a lateral hook, on which the thermometer is hung.

A layer of mercury, about 15 mm. high, is first put into the outer cylinder *b*. The measuring cylinder is perfectly filled with mercury, and inverted in a shallow mercurial trough. A weighed quantity of the fluid to be vaporized in a bulb of thin glass (fig. 99) is now placed underneath the opening of the measuring cylinder, and allowed to ascend; the cylinder *a* is then transported to *b*, with the aid of a long-handled iron spoon, of the same form as is in general use for combustions in oxygen.

Fig. 99.

The bursting of the bulb and the formation of vapor are next brought about by filling the outer cylinder *b* cautiously and up to the top with a hot fluid. According to the boiling point of the substance we use for this purpose either boiling water, or some saline solution, preferably dilute glycerine or a solution of chloride of calcium in dilute glycerine. The specific gravity of the hot fluid is to be determined in a suitable manner (according to H. **Schiff**, by means of an areometer). The outer cylinder stands on a strong low tripod in a small glass trough; the latter serves to receive the fluid, which is ejected by the vapor as it forms; it is, moreover, filled nearly up to the level of the mercury in the outer cylinder with the hot fluid, in order that the mercury may be raised to the same temperature. After a few minutes the rate of cooling will have become so much slower that the volume of the vapor may be considered stationary. Finally, the pressure and temperature are noted, also the height of the mercury in the measuring tube, and in the outer cylinder (the latter being read off on the scale of the measuring tube).

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* Zeitschrift f. analyt. Chem. 1, 320.

C. The determination of the vapor densities of bodies of high boiling points is made after the method of DEVILLE and TROOST,* for a description of which I must refer the reader to the original memoir.

§ 192.

3. A great many indifferent organic bodies absolutely refuse to combine with bases or acids; or only form with them compounds, from which the equivalent of the organic body cannot well be determined. The equivalent of such substance is determined by producing by the action of acids, bases, halogens, &c., upon the body under examination, new compounds of known or ascertainable equivalents. Or, lastly, the equivalent is inferred from the manner in which the compound in question has been formed. In cases of this description, that equivalent is assumed to be the correct one which permits the most simple explanation of the processes of formation and decomposition.

This mode of determining the equivalent of substances is intimately connected with the higher branches of organic chemistry, and cannot be considered in detail here, as it is impossible to give universally applicable methods.

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* Compt. Rend. 49, 239; Annal. d. Chem. u. Pharm. 113, 42.

DIVISION II.

CALCULATION OF ANALYSES.

The calculation of the results obtained by an analysis presupposes, as an indispensable preliminary, a knowledge of the general laws of the combining proportions of bodies, on the one hand, and of the more simple rules of arithmetic on the other. It is a great error to suppose that the ability to make chemical calculations involves an extensive acquaintance with mathematics, a knowledge of decimal fractions and simple equations being for the most part sufficient. These remarks are not intended to dissuade students of chemistry from pursuing the highly important study of mathematics; but merely to encourage those who have had no opportunity of entering more deeply into this science, and who, as experience has shown me, are often afraid to venture upon chemical calculations. For this reason, I have made the whole of the calculations given in the following paragraphs, in the most intelligible manner possible, and without logarithms.

I. *Calculation of the Constituent sought from the Compound obtained in the Analytical Process, and exhibition of the Result in Per-cents.*

§ 193.

The bodies the weight of which it is intended to determine, are separated, as we have seen in Division I., treating of the "Execution of Analysis," either in the free state, or—and this most frequently—in combinations of known composition. The results are usually calculated upon 100 parts of the examined substance, since this gives a clearer and more intelligible view of the composition. In cases where the several constituents have been separated in the free state, the calculation may be made at once; but if the constituents have been separated in combination with other substances, they must first be calculated from the compounds obtained.

1. *Calculation of the Results into Per-cents by Weight, in Cases where the Substance sought has been separated in the Free State.*

a. Solid Bodies, Liquids, and Gases, which have been determined by Weight.

§ 194.

The calculation here is exceedingly simple.

Suppose you have analyzed subchloride of mercury, and separated the mercury in the metallic state (§ 118, 1). 2·945 grm. subchloride of mercury have given say 2·499 grm. metallic mercury.

$$2{\cdot}945 : 2{\cdot}499 :: 100 : x$$
$$x = 84{\cdot}85,$$

which means that your analysis shows 100 parts of subchloride of mercury to contain 84·85 of mercury, and consequently 15·15 of chlorine.

Now as the subchloride of mercury is known to consist of 2 eq. mercury and 1 eq. chlorine, and as the equivalent numbers of both these elements are also known, the true percentage composition of the body may be readily calculated from these data. When analyzing substances of known composition for practice, the results theoretically calculated and those obtained by the analysis are usually placed in juxtaposition, as this enables the student at once to perceive the degree of accuracy with which the analysis has been performed.

Thus for instance—

	Found.	Calculated (compare § 84, *b*).
Mercury	84·85	84·94
Chlorine	15·15	15·06
	100·00	100·00

b. Gases which have been determined by Measure.

§ 195.

If a gas has been determined by measure, it is, of course, necessary first to ascertain the weight corresponding to the volume found, before the percentage by weight can be calculated.

But as the exact weights of a definite volume of the various gases have been severally determined by accurate experiments, this calculation also is a simple rule-of-three question, if the gas may be measured under the same circumstances to which the known relation of weight to volume refers. The circumstances to be taken into consideration here, are:

Temperature and Atmospheric Pressure.

Besides these, the

Tension of the Aqueous Vapor

may also claim consideration in cases where water is used as the confining fluid, or generally where the gas has been measured in the moist state.

The respective weights assigned in Table V.* to 1 litre of the gases there enumerated, refer to a temperature of 0°, and an atmospheric pressure of 0·76 metre of mercury. We have, therefore, in the first place, to consider the manner in which volumes of gas measured at another temperature and another height of the barometer, are to be reduced to 0° and 0·76 of the barometer.

α. Reduction of a Volume of Gas of any given Temperature to 0°, *or any other Temperature between* 0° *and* 100°.

The following propositions regarding the expansion of gases were formerly universally adopted:—

1. All gases expand alike for an equal increase of temperature.

2. The expansion of one and the same gas for each degree of the thermometer is independent of its original density.

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* See Tables at the end of the volume.

Although the correctness of these propositions has not been fully confirmed by the minute investigations of MAGNUS and REGNAULT, yet they may be safely followed in reductions of the temperature of those gases which are most frequently measured in the course of analytical processes, as the coefficients of expansion of these gases scarcely differ from each other, and as there is never any very considerable difference in the atmospheric pressure under which the gases are severally measured.

The investigations just alluded to have given

$$0{\cdot}3665$$

as the coefficient of the expansion of gases which comes nearest to the truth; in other words, as the extent to which gases expand when heated from the freezing to the boiling point of water. They expand, therefore, for every degree of the centigrade thermometer,

$$\frac{0{\cdot}3665}{100}=0{\cdot}003665.$$

If we wish to ascertain how much space 1 c. c. of gas at 0° will occupy at 10°, we find

$$1\times[1+(10\times 0{\cdot}003665)]=1{\cdot}03665.$$

If we wish to ascertain how much space 100 c. c. at 0° will occupy at 10°, we find

$$\begin{aligned}&100\times[1+(10\times 0{\cdot}003665)]\\=&100\times 1{\cdot}03665-103{\cdot}665.\end{aligned}$$

If we wish to know how much space 1 c. c. at 10° will occupy at 0°, we find

$$\frac{1}{1+(10\times 0{\cdot}003665)}=0{\cdot}965.$$

How much space do 103·665 c. c. at 10° occupy at 0°?

$$\frac{103{\cdot}665}{1+(10\times 0{\cdot}003665)}=100.$$

The general rule of these calculations may be expressed as follows:—

To calculate the volume of a gas from a lower to a higher temperature, we have in the first place to find the expansion for the volume unit, which is done by adding to 1 the product of the multiplication of the thermometrical difference by 0·003665; and then to multiply this by the number of volume units found in the analytical process. On the other hand, to reduce the volume of a gas from a higher to a lower temperature, we have to divide the number of volume units found in the analytical process, by 1 + the product of the multiplication of the thermometrical difference by 0·003665.

β. *Reduction of the Volume of a Gas of a certain given Density to ·76 Metre Barometric Pressure, or any other given Pressure.*

According to the law of MARIOTTE, the volume of a gas is inversely as the pressure to which it is exposed; in accordance with this, a gas occupies the greater space the less the pressure upon it, and the less space the greater the pressure upon it.

Thus, supposing a gas to occupy a space of 10 c. c. at a pressure of

1 atmosphere, it will occupy 1 c. c. at a pressure of 10 atmospheres, and 100 c. c. at a pressure of $\frac{1}{10}$ atmosphere.

Nothing, therefore, can be more easy than the reduction of a gas of a certain given tension to 760 mm. bar. pressure, or any other given pressure, *e.g.*, 1000 mm., which is frequently used in the analysis of gases.

Supposing a gas to occupy 100 c. c. at 780 mm. bar., how much space will it occupy at 760 mm.?

$$760 : 780 :: 100 : x$$
$$x = 102{\cdot}63.$$

How much space will 100 c. c. at 750 mm. bar. occupy at 760 mm.?

$$760 : 750 :: 100 : x$$
$$x = 98{\cdot}68.$$

How much space will 150 c. c. at 760 mm. bar. occupy at 1000 mm.?

$$1000 : 760 :: 150 : x$$
$$x = 114.$$

γ. *Reduction of the Volume of a Gas saturated with Aqueous Vapor, to its actual Volume in the Dry State.*

It is a well-known fact that water has a tendency, at all temperatures, to assume the gaseous state. The degree of this tendency (the tension of the aqueous vapor)—which is dependent solely and exclusively upon the temperature, and not upon the circumstance of the water being *in vacuo* or in any gaseous atmosphere—is usually expressed by the height of a column of mercury counterbalancing it. The following table indicates the amount of tension for the various temperatures at which analyses are likely to be made.*

TABLE.

Temperature (in degrees C.)	Tension of the aqueous vapor expressed in millimetres.	Temperature (in degrees C.)	Tension of the aqueous vapor expressed in millimetres.
0	4·525	21	18·505
1	4·867	22	19·675
2	5·231	23	20·909
3	5·619	24	22·211
4	6·032	25	23·582
5	6·471	26	25·026
6	6·939	27	26·547
7	7·436	28	28·148
8	7·964	29	29·832
9	8·525	30	31·602
10	9·126	31	33·464
11	9·751	32	35·419
12	10·421	33	37·473
13	11·130	34	39·630
14	11·882	35	41·893
15	12·677	36	44·268
16	13·519	37	46·758
17	14·409	38	49·368
18	15·351	39	52·103
19	16·345	40	54·969
20	17·396		

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* Compare Magnus, Pogg. Annal. 61, 247.

Therefore, if a gas is confined over water, its volume is, *cæteris paribus*, always greater than if it were confined over mercury; since a quantity of aqueous vapor, proportional to the temperature of the water, mixes with the gas, and the tension of this partly counterbalances the column of air that presses upon the gas, and to that extent neutralizes the pressure. To ascertain the actual pressure upon the gas, we must therefore subtract from the apparent pressure so much as is neutralized by the tension of the aqueous vapor.

Suppose we had found a gas to measure 100 c. c. at 759 mm. bar., the temperature of the confining water being 15°; how much space would this volume of gas occupy in the dry state and at 760 mm. of the barometer?

Our table gives the tension of aqueous vapor at 15° = 12·677; the gas is consequently not under the apparent pressure of 759 mm., but under the actual pressure of 759 − 12·677 = 746·323 mm.

The calculation is now very simple; it proceeds in the manner shown in β; we say,

$$760 : 746{\cdot}323 :: 100 : x$$
$$x = 98{\cdot}20.$$

When the volume of a gas has thus been adjusted by the calculations in α and β, or γ, to the thermometrical and barometrical conditions to which the data of Table V. refer, the percentage by weight may now be readily calculated by substituting the weight for the volume, and proceeding by simple rule of three.

What is the percentage by weight of nitrogen in an analyzed substance, of which 0·5 grm. have yielded 30 c. c. of dry nitrogen gas at 0°, and 760 mm. bar.?

In Table V. we find that 1 litre (1000 c. c.) of nitrogen gas at 0°, and 760 mm. bar., weighs 1·25456 grm.

We say accordingly:

$$1000 : 1{\cdot}25456 :: 30 : x$$
$$x = 0{\cdot}0376.$$

And then:

$$0{\cdot}5 : 0{\cdot}0376 :: 100 : x$$
$$x = 7{\cdot}52.$$

The analyzed substance contains consequently 7·52 per cent. by weight of nitrogen.

2. *Calculation of the Results into Per-cents by Weight, in Cases where the Body sought has been separated in Combination, or where a Compound has to be determined from one of its Constituents.*

§ 196.

If the body to be determined has not been weighed or measured in its own form, but in some other form, *e.g.*, carbonic acid as carbonate of lime, sulphur as sulphate of baryta, ammonia as nitrogen, chlorine by a standard solution of iodine, &c., its quantity must first be reckoned from that of the compound found before the calculation described in 1 can be made.

This may be accomplished either by rule of three or by some abridged method.

Suppose we have weighed hydrogen in the form of water, and have found 1 grm. of water; how much hydrogen does this contain?

An equivalent of water consists of:

1 of hydrogen
8 of oxygen
9 water.

We say accordingly:

$$9 : 1 :: 1 : x$$
$$x = 0{\cdot}11111.$$

From the above proportion results the following equation:

$$\frac{1}{9} \times 1 = x,$$

or

$$0{\cdot}11111 \times 1 = x.$$

Or, expressed in general terms:

Water × 0·11111 = *Hydrogen.*

EXAMPLE.—

517 of water; how much hydrogen?
517 × 0·11111 = 57·444.

The following equation results also from the above proportion:

$$\frac{9}{1} = \frac{1}{x}$$
$$9 = \frac{1}{x}$$
$$\therefore \; x = \frac{1}{9}$$

Or, expressed in general terms,

Water divided by 9 = *Hydrogen.*

EXAMPLE.—

517 of water, how much hydrogen?

$$\frac{517}{9} = 57{\cdot}444.$$

In this manner we may find for every compound constant numbers by which to multiply or divide the weight of the compound, in order to find the weight of the constituent sought (comp. Table III.*).

Thus, for instance, the nitrogen may be obtained from the double bichloride of platinum and chloride of ammonium, by dividing the weight of the latter by 15·96, or multiplying it by 0·06269; thus the carbon may be calculated from the carbonic acid by multiplying the weight of the latter by 0·2727, or dividing it by 3·666.

These numbers are by no means so simple, convenient, and easy to remember as in the case of hydrogen. It is therefore advisable, in the case of carbonic acid, for instance, to fix upon another general expression, viz.,

$$\frac{\textit{Carbonic acid} \times 3}{11} = \textit{Carbon};$$

---

[*] See Tables at the end of the volume.

which is derived from the proportion

22 : 6 :: the carbonic acid found : x.

The object in view may also be attained in a very simple manner, by reference to table IV.,* which gives the amount of the constituent sought for every number of the compound found, from 1 to 9; the operator need, therefore, simply add the several values together.

As regards hydrogen, for instance, we find :—

TABLE.

Found.	Sought.	1	2	3	4	5	6	7	8	9
water	hydrogen	0·11111	0·22222	0·33333	0·44444	0·55555	0·66667	0·77778	0·88889	1·00000

From this table it is seen that 1 part of water contains 0·11111 of hydrogen, that 5 parts of water contain 0·55555 of hydrogen; 9 parts, 1·00000, &c.

Now if we wish to know, for instance, how much hydrogen is contained in 5·17 parts of water, we find this by adding the values for 5 parts, for $\frac{1}{10}$ part, and for $\frac{7}{100}$ parts, thus :—

$$\begin{array}{l} 0{\cdot}55555 \\ 0{\cdot}011111 \\ \underline{0{\cdot}0077778} \\ 0{\cdot}5744388 \end{array}$$

Why the numbers are to be placed in this manner, and not as follows :—

$$\begin{array}{l} 0{\cdot}55555 \\ 0{\cdot}11111 \\ \underline{0{\cdot}77778} \\ 1{\cdot}44444 \end{array}$$

is self-evident, since arranging them in the latter way would be adding the value for 5, for 1, and for 7 (5 + 1 + 7 = 13) and not for 5·17. This reflection shows also that, to find the amount of hydrogen contained in 517 parts of water, the points must be transposed as follows :—

$$\begin{array}{r} 55{\cdot}555 \\ 1{\cdot}1111 \\ \underline{0{\cdot}77778} \\ 57{\cdot}44388 \end{array}$$

3. *Calculation of the Results of Indirect Analyses into Per-Cents by Weight.*

§ 197.

The import of the term "*indirect analysis*," as defined in § 151, p. 337, shows sufficiently that no universally applicable rules can be laid down for the calculations which have to be made in indirect analyses. The selection of the right way must be left in every special case to the intelligence of the analyst. I will here give the mode of calculating the results in the more important indirect separations described in Section V. They may serve as examples for other similar calculations.

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* See Tables at the end of the volume.

a. Indirect Determination of Soda and Potassa.

This is effected by determining the sum total of the chlorides, and the chlorine contained in them.

The calculation may be made as follows:

Suppose we have found 3 grm. of chloride of sodium and chloride of potassium, and in these 3 grm. 1·6888 of chlorine.

Eq. Chlorine.		Eq. K Cl.		Chlorine found.
35·46	:	74·57	::	1·6888 : x
		x	=	3·5514.

If all the chlorine present were combined with potassium, the weight of the chloride would amount to 3·5514. As the chloride weighs less, chloride of sodium is present, and this in a quantity proportional to the difference (*i.e.*, 3·5514—3=0·5514), which is calculated as follows:—

The difference between the equivalent of K Cl and that of Na Cl (16·11) is to the equivalent of Na Cl (58·46), as the difference found is to the chloride of sodium present:—

$$16{\cdot}11 : 58{\cdot}46 :: 0{\cdot}5514 : x$$
$$x = 2\ \mathrm{Na\,Cl}$$
$$\text{and } 3-2=1\ \mathrm{K\,Cl}.$$

From this the following short rule is derived:—

Multiply the quantity of chlorine in the mixture by 2·1029, deduct from the product the sum of the chlorides, and multiply the remainder by 3·6288; the product expresses the quantity of chloride of sodium contained in the mixed chloride.

The calculation may also be made by help of the subjoined formulæ (COLLIER*).

W=weight of mixed chlorides
C= " " chlorine.

$$\mathrm{Na\,Cl} = C\times 7{\cdot}6311) - (W\times 3{\cdot}6288)$$
$$\mathrm{K\,Cl} = (W\times 4{\cdot}6288) - (C\times 7{\cdot}6311)$$
$$\mathrm{Na\,O} = (C\times 4{\cdot}0466) - (W\times 1{\cdot}9243)$$
$$\mathrm{K\,O} = (W\times 2{\cdot}9243) - (C\times 4{\cdot}8210).$$

b. Indirect Determination of Strontia and Lime.

This may be effected by determining the sum total of the carbonates, and the carbonic acid contained in them (§ 154, 7). Suppose we have found 2 grm. of mixed carbonate, and in these 2 grm. 0·7383 of carbonic acid.

Eq. $C\,O_2$		Eq. $Sr O,\ C\,O_2$		$C\,O_2$ found.
22	:	73·75	::	0·7383 : x
		x	=	2·47498.

If, therefore, the whole of the carbonic acid were combined with strontia, the weight of the carbonate would amount to 2·47498 grm. The deficiency,=0·47498 is proportional to the carbonate of lime present, which is calculated as follows:—

The difference between the equivalent of $Sr\,O,\ C\,O_2$, and the equivalent of $Ca\,O, C\,O_2$ (23·75) is to the equivalent of $Ca\,O, C\,O_2$ (50), as the difference found is to the carbonate of lime contained in the mixed salt:—

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* Am. Jour. Sci., March, 1864, p. 346.

$$\therefore \quad 23{\cdot}75 : 50 :: 0{\cdot}47498 : x$$
$$x = 1.$$

The mixture, therefore, consists of 1 grm. carbonate of lime and 1 grm. carbonate of strontia.

From this the following short rule is derived:—

Multiply the carbonic acid found by 3·3523, deduct from the product the sum of the carbonates, and multiply the difference by 2·10526; the product expresses the quantity of the carbonate of lime.

c. *Indirect Determination of Chlorine and Bromine* (§ 169, 1).

Let us suppose the mixture of chloride and bromide of silver to have weighed 2 grm., and the diminution of weight consequent upon the transmission of chlorine to have amounted to 0·1 grm. How much chlorine is there in the mixed salt, and how much bromine?

The decrease of weight here is simply the difference between the weight of the bromide of silver originally present, and that of the chloride of silver which has replaced it; if this is borne in mind, it is easy to understand the calculation which follows:—

The difference between the equivalents of bromide of silver and chloride of silver is to the equivalent of bromide of silver as the ascertained decrease of weight is to x, *i.e.*, to the bromide of silver originally present in the mixture:—

$$\therefore \quad 44{\cdot}54 : 187{\cdot}97 :: 0{\cdot}1 : x$$
$$x = 0{\cdot}422025.$$

The 2 grm. of the mixture therefore contained 0·422025 grm. bromide of silver, and consequently 2 − 0·422025 = 1·577975 grm. chloride of silver.

It results from the above, that we need simply multiply the ascertained decrease of weight by

$$\frac{187{\cdot}97}{44{\cdot}54}\, i.e., \text{ by } 4{\cdot}22025$$

to find the amount of bromide of silver originally present in the analyzed mixture. And if we know this, we also know of course the amount of the chloride of silver; and from these data we deduce the quantities of chlorine and bromine, as directed in § 196, and the percentages as directed in § 193.

SUPPLEMENT TO I.

REMARKS ON LOSS AND EXCESS IN ANALYSES, AND ON TAKING THE AVERAGE.

§ 198.

If, in the analysis of a substance, one of the constituents is estimated from the loss, or, in other words, by subtracting from the original weight of the analyzed substance the ascertained united weight of the other constituents, it is evident that in the subsequent percentage calculation the sum total must invariably be 100. Every loss suffered or excess obtained in the determination of the several constituents will, of course, fall exclusively upon the one constituent which is estimated from the loss. Hence estimations of this kind cannot be considered accurate, unless the other constituents have been determined by good methods, and with the greatest care. The accuracy of the results will, of course, be the greater, the less the number of constituents determined in the direct way.

If, on the other hand, every constituent of the analyzed compound has been determined separately, it is obvious that, were the results absolutely accurate, the united weight of the several constituents must be exactly equal to the original weight of the analyzed substance. Since, however, as we have seen in § 96, certain inaccuracies attach to every analysis, without exception, the sum total of the results in the percentage calculation will sometimes exceed, and sometimes fall short of, 100.

In all cases of this description, the only proper way is to give the results as actually found.

Thus, for instance, PELOUZE found, in his analysis of chromate of chloride of potassium,

Potassium	21·88
Chlorine	19·41
Chromic acid	58·21
	99·50

BERZELIUS, in his analysis of sesquioxide of uranium and potassa,

Potassa	12·8
Sesquioxide of uranium	86·8
	99·6

PLATTNER, in his analysis of pyrrhotine,

	Of Fahlun.	Of Brasil.
Iron	59·72	59·64
Sulphur	40·22	40·43
	99·94	100·07

It is altogether inadmissible to distribute any chance deficiency or excess proportionately among the several constituents of the analyzed compound, as such deficiency or excess of course never arises from the several estimations in the same measure; moreover, such "doctoring" of the analysis deprives other chemists of the power of judging of its accuracy. No one need be ashamed to confess having obtained somewhat too little or somewhat too much in an analysis, provided, of course, the deficiency or excess be confined within certain limits, which differ in different analyses, and which the experienced chemist always knows how to fix properly.

In cases where an analysis has been made twice, or several times, it is usual to take the mean as the most correct result. It is obvious that an average of the kind deserves the greater confidence the less the results of the several analyses differ. The results of the several analyses must, however, also be given, or, at all events, the maximum and minimum.

Since the accuracy of an analysis is not dependent upon the quantity of substance employed (provided always this quantity be not altogether too small), the average of the results of several analyses is to be taken quite independently of the quantities used; in other words, you must not add together the quantities used, on the one hand, and the weights obtained in the several analyses on the other, and deduce from these data the percentage amount; but you must calculate the latter from the results of each analysis separately, and then take the mean of the numbers so obtained.

Suppose a substance, which we will call AB, contains fifty per cent. of A; and suppose two analyses of this substance have given the following results:

(1) 2 grm. AB gave 0·99 grm. of A.
(2) 50 " " 24·00 "

From 1, it results that AB contains 49·50 per cent. of A.
" 2, " " 48·00 "

Total . . . . 97·50
Mean . . . . 48·75

It would be quite erroneous to say

$$2+50=52 \text{ of AB gave } 0{\cdot}99+24{\cdot}00=24{\cdot}99 \text{ of A,}$$

therefore 100 of AB contain 48·06 of A;

for it will be readily seen that this way of calculating destroys nearly altogether the influence of the more accurate analysis (1) upon the average, on account of the proportionally small amount of substance used.

II. Deduction of Empirical Formulæ.

§ 199.

If the percentage composition of a substance is known, a so-called empirical formula may be deduced from this; in other words, the relative proportion of the several constituents may be expressed in equivalents—in a formula which, upon recalculation in per-cents will give numbers corresponding perfectly, or nearly, with those obtained by the analysis. We are compelled to confine ourselves to the expression of empirical formulæ, in the case of all substances of which we cannot determine the equivalent, as *e.g.*, woody fibre, mixed substances, &c.

The method of deducing empirical formulæ is very simple, and will be readily understood from the following reflections:—

How should we proceed to find the relative number of equivalents in carbonic acid?

We should say:—

The equivalent of the oxygen is to the amount of oxygen in the equivalent of carbonic acid, as 1 is to x, *i.e.*, to the number of equivalents of oxygen contained in carbonic acid;

$$\therefore \quad 8 : 16 :: 1 : x$$
$$x=2.$$

In the same manner we should find the number of equivalents of carbon by the following proportion:—

$6 : 6 :: 1 : x$

(equivalent of carbon) (carbon in one equivalent of carbonic acid)

$x=1.$

Now let us suppose we did not know the equivalent of carbonic acid, but simply its percentage composition, viz.,

27·273 carbon
72·727 oxygen

100·000 carbonic acid;

the relative proportion of the equivalents might still be ascertained, even though any other given number, say 100, be selected for the equivalent of carbonic acid. Let us suppose we adopt 100 as the equivalent of carbonic acid; thus,

$8 : 72{\cdot}727 :: 1 : x$

(Eq. O) (Amount of oxygen in the assumed eq. 100)

$x=9{\cdot}0910$

and

$6 : 27{\cdot}273 :: 1 : x$

(Eq. C) (Amount of carbon in the assumed eq. 100)

$x=4{\cdot}5455.$

We see here that although the *numbers* which express the relative proportion of the equivalents of oxygen and carbon have changed, yet the *relative proportion* itself remains the same; since

$4{\cdot}5455 : 9{\cdot}0910 :: 1 : 2.$

The process may accordingly be expressed in general terms as follows:

Assume any number, say 100 (because this is the most convenient), as the equivalent of the compound, and ascertain how often the equivalent of each constituent severally is contained in the amount of the same constituent present in 100 parts. When you have thus found the numbers expressing the relative proportion of the equivalents, you have attained your purpose—viz., the deduction of an empirical formula. Still, it is usual to reduce the numbers found to the simplest expression.

Now let us take a somewhat complicated case, *e.g.*, the deduction of the empirical formula for mannite.

The percentage composition of mannite is

39·56 of carbon
7·69 of hydrogen
52·75 of oxygen

100·00

This gives the following proportions:

$6 : 39{\cdot}56 :: 1 : x$ $x=6{\cdot}593$
$1 : 7{\cdot}69 :: 1 : x$ $x=7{\cdot}690$
$8 : 52{\cdot}75 :: 1 : x$ $x=6{\cdot}593$

We have now the empirical formula for mannite, viz.,

$$C_{6·593} \qquad H_{7·690} \qquad O_{6·593}$$

A glance shows that the number of the equivalents of the carbon is equal to that of the equivalents of the oxygen; and the question is now whether the relative proportion found may not be expressed by smaller numbers.

A simple calculation suffices to answer this question, viz.,

$$6·593 : 7·690 :: 60 : x$$

(Any other number might be substituted for 60, as the third term of the proportion, but 60 is very suitable, since it is divisible without remainder by most of the numbers.)

$$x = 70$$

We have accordingly now the simple formula,

$$C_{60} \ H_{70} \ O_{60} = C_6 \ H_7 \ O_6.$$

The percentage composition of mannite given above having been calculated from the formula, of course the latter is evolved again without ambiguity. Now let us take the results of an actual analysis.

OPPERMANN obtained, upon the combustion of 1·593 grm. mannite, with oxide of copper, 2·296 carbonic acid and 1·106 water. This gives in per-cents,

39·31	carbon
7·71	hydrogen
52·98	oxygen
100·00	

which, calculated as above, gives

$$C_{6·552} \qquad H_{7·710} \qquad O_{6·622}$$

as the first expression of the empirical formula; and by the proportion:

$$6·552 : 7·710 = 6 : x$$
$$x :: 7·06$$

A glance at these numbers shows that 7·06 may be properly exchanged for 7, and also that the difference between 6·552 and 6·622 is so trifling that both may be expressed by the same number. These considerations lead therefore likewise to the formula

$$C_6 \ H_7 \ O_6$$

The proof whether the formula is correct or not is obtained by its recalculation in per-cents. The less the calculated percentage differs from that found, the more reason there is to believe in the correctness of the formula. If the difference is more considerable than can be accounted for by the defects inherent in the methods, there is every reason to believe the formula fallacious, in which case it is necessary to establish a more correct one; for it will be readily seen that, in the case of substances of which the equivalent is not known, different formulae may be deduced from one and the same analysis, or from several very nearly corresponding analyses; since the numbers found are never absolutely correct, but only approximate.

Thus, for instance, in the case of mannite:

	Calculated			Found
for		for		
C_6	39·56	C_8	39·67	39·31
H_7	7·69	H_9	7·44	7·71
O_6	52·75	O_8	52·89	52·98
	100·00		100·00	100·00

III. Deduction of Rational Formulæ.

§ 200.

If both the percentage composition and the equivalent of a substance are known, it is easy to deduce its *rational* formula—that is, a formula expressing not only the relative proportion of the equivalents, but also their absolute number.

The following examples may serve for illustration:—

1. *Deduction of the Rational Formula of Hyposulphuric Acid.*

Analysis has given, in the first place, the percentage composition of hyposulphuric acid, and, in the second place, the percentage composition of hyposulphate of potassa, viz.,

Sulphur	44·44	Potassa	39·551
Oxygen	55·56	Hyposulphuric acid .	60·449
Hyposulphuric acid .	100.00	Hyposulphate of potassa	100·000

(Equivalent of potassa=47·11)

Now:

$$39{\cdot}551 : 60{\cdot}449 :: 47{\cdot}11 : x \qquad x=72$$

Hence 72 is the sum of the equivalents of the constituents contained in hyposulphuric acid—in other terms, the equivalent of hyposulphuric acid.

Having thus ascertained the correct equivalent of hyposulphuric acid, it is unnecessary to assume a hypothetical one, as we are obliged to do in the case of mannite.

Thus we may state at once:

$$100 : 44{\cdot}44 :: 72 : x \qquad x=32;$$

i.e.=the sum of the equivalents of the sulphur; and again:

$$100 : 55{\cdot}56 :: 72 : x \qquad x=40;$$

i.e.=the sum of the equivalents of the oxygen.

Now the equivalent of sulphur, *i.e.* 16, is contained twice in 32; and the equivalent of oxygen, *i.e.* 8, is contained five times in 40; the rational formula for hyposulphuric acid is accordingly,

$$S_2\,O_5.$$

2. *Deduction of the Rational Formula of Benzoic Acid.*

Stenhouse obtained from 0·3807 hydrated benzoic acid, dried at 100°, 0·9575 carbonic acid and 0·1698 water.

0·4287 benzoate of silver, dried at 100°, gave 0·202 silver. From these numbers result the following percentage compositions:—

Carbon	68·67
Hydrogen	4·95
Oxygen	26·38
Hydrated benzoic acid	100·00

Oxide of silver	50·67
Benzoic acid	49·33
Benzoate of silver	100·00

(Equivalent of the oxide of silver=115·97)

$50{\cdot}67 : 49{\cdot}33 :: 115{\cdot}97 : x \qquad x=112{\cdot}904$

i.e. the equivalent of anhydrous benzoic acid; that of the hydrated acid accordingly=112·904+9=121·904; we say therefore now

$100 : 68{\cdot}67 :: 121{\cdot}904 : x \qquad x=83{\cdot}711$
$100 : 4{\cdot}95 :: 121{\cdot}904 : x \qquad x=6{\cdot}035$
$100 : 26{\cdot}38 :: 121{\cdot}904 : x \qquad x=32{\cdot}158$

6	is contained in	83·711	13·95 times
1	"	6·035	6·03 "
8	"	32·158	4·02 "

A glance at these quotients suffices to show that 13·95 may be exchanged for 14, 6·03 for 6, and 4·02 for 4. The rational formula for the hydrate of benzoic acid is accordingly,

$$C_{14}\ H_6\ O_4.$$

	This gives, by calculation,	The numbers found were,
C	68·85	68·67
H	4·92	4·95
O	26·23	26·38
	100·00	100·00

3. *Deduction of the Rational Formula of Theine.*

Stenhouse's analysis of theine, free from water of crystallization, gave the following results:—

1. 0.285 grm. substance gave 0·5125 carbonic acid and 0·132 water.
2. Combustion with oxide of copper gave a mixture of CO_2 and N, in the proportion of 4 of the former to 1 of the latter.
3. 0·5828 grm. of the double salt of hydrochlorate of theine and bichloride of platinum, gave 0·143 platinum.

From these numbers results the following percentage composition:—

Carbon	49·05
Hydrogen	5·14
Nitrogen	28·61
Oxygen	17·20
	100·00

and 196·91 as the equivalent of theine. For there is every reason to suppose that the composition of the double salt of hydrochlorate of theine and bichloride of platinum is

$$\text{Theine} + H\,Cl + Pt\,Cl_2$$

The equivalent of this double salt is found by the following proportion:

$$0·143 : 0·5828 :: 98·94 \text{ (eq. platinum)} : x \qquad x=403·23;$$

and consequently the equivalent of theine, by subtracting from 403·23 the sum of 1 eq. bichloride of platinum (169·86) and 1 eq. hydrochloric acid (36·46)

$$403·23-(169·86\times 36·46)=196·91.$$

This supplies the following proportions:—

$100 : 49·05 :: 196·91 : x \qquad x=96·584$
$100 : 5·14 :: 196·91 : x \qquad x=10·121$
$100 : 28·61 :: 196·91 : x \qquad x=56·336$
$100 : 17·20 :: 196·91 : x \qquad x=33·868$

6 is contained in 96·584, 16·09 times
1 " 10·121, 10·12 "
14 " 56·336, 4·02 "
8 " 33·868, 4·23 "

for which numbers may be substituted, 16, 10, 4, and 4, respectively, and we get the following formula:

$$C_{16}\,H_{10}\,N_4\,O_4$$

This gives by calculation,	Found.
C 49·47	49·05
H 5·15	5·14
N 28·89	28·61
O 16·49	17·20
100·00	100·00

The double hydrochlorate of theine and bichloride of platinum gives platinum in 100 parts,

Calculated.	Found.
24·70	24·53

4. *Special Method of Deducing Rational Formulæ for Oxygen Salts.*

a. In the case of Compounds containing no Isomorphous Constituents.

The rational formulæ for oxygen salts may be deduced also by a method different from the foregoing, viz., by ascertaining the ratio which the respective quantities of oxygen bear to each other. This method is exceedingly simple.

In an analysis of crystallized sulphate of soda and ammonia, I found,

Soda	17·93
Oxide of ammonium .	15·23
Sulphuric acid . .	46·00
Water . .	20·84
	100·00

31 of NaO contain 8 of O, consequently 17·93 of NaO contain 4·63 of O.
26 .. NH_4O .. 8 .. O, .. 15·23 .. NH_4O .. 4·68 .. O.
40 .. SO_3 .. 24 .. O, .. 46·00 .. SO_3 .. 27·60 .. O.
9 .. HO .. 8 .. O, .. 20·84 .. HO .. 18·52 .. O.

Now

$$4{\cdot}63 : 4{\cdot}68 : 27{\cdot}60 : 18{\cdot}52 = 1 : 1{\cdot}01 : 5{\cdot}97 : 4{\cdot}00 = 1 : 1 : 6 : 4,$$

and this leads to the formula

$$Na\,O, N\,H_4\,O, 2\,S\,O_3 \times 4\,H\,O$$
$$\text{or, } Na\,O, S\,O_3 + N\,H_4\,O, S\,O_3 + 4\text{ aq.}$$

b. In the case of Compounds containing Isomorphous Constituents.

It is a well-known fact that isomorphous constituents may replace each other in all proportions; therefore, in establishing a formula for compounds containing isomorphous constituents, the latter are taken *collectively*; that is, they are expressed in the formula as *one and the same body*. This very frequently occurs in the calculation of formulæ for minerals.

A. ERDMANN found in monradite

			Amount of Oxygen.
Silicic acid	56·17	. . . .	29·957
Magnesia	31·63	. 12.652	14.601
Protoxide of iron	8·56	. 1·949	
Water	4·04	. . . .	3·590
	100·40		

Now

$$3{\cdot}59 : 14{\cdot}601 : 29{\cdot}957 = 1 : 4{\cdot}07 : 8{\cdot}3 = 1 : 4 : 8.$$

Designating 1 eq. metal by R, we obtain from these numbers the formula:—

$$4\,(R\,O, Si\,O_2) + HO \text{ or } 4\left(\left.\begin{matrix}Mg\\Fe\end{matrix}\right\} O, Si\,O_2\right) + \text{aq.}$$

Not only isomorphous substances, but generally all bodies of analogous composition possess the faculty of replacing each other in compounds; thus we find that KO, Na O, Ca O, Mg O, &c., replace each other. These substances likewise must be expressed collectively in the formula.

ABICH found in andesine

			Amount of Oxygen.
Silicic acid	59·60	. . . . .	31·79
Alumina	24·28	. . 11·22	11·70
Sesquioxide of iron	1·58	. . 0·48	
Lime	5·77	. . 1·61	3·90
Magnesia	1·08	. . 0·43	
Soda	6·53	. . 1·68	
Potassa	1·08	. . 0·18	
	99·92		

Now

$$3{\cdot}90 : 11{\cdot}70 : 31{\cdot}79 = 1 : 3 : 8{\cdot}15 = 1 : 3 : 8.$$

Designating 1 eq. metal by R, we obtain from these numbers the formula:—

$$R\,O + R_2\,O_3 + 4\,Si\,O_2$$
$$= R\,O, Si\,O_2 + R_2\,O_3, 3\,Si\,O_2,$$

which may likewise be written:—

$$\left.\begin{matrix}\mathrm{Ca}\\ \mathrm{Mg}\\ \mathrm{Na}\\ \mathrm{K}\end{matrix}\right\}\mathrm{O, Si\,O_2} + \left.\begin{matrix}\mathrm{Al_2}\\ \mathrm{Fe_2}\end{matrix}\right\}\mathrm{O_3, 3\,Si\,O_2}.$$

Showing thus that this mineral is leucite ($K\,O, Si\,O_2 + Al_2\,O_3, 3\,Si\,O_2$), in which the greater part of the potassa is replaced by lime, soda, and magnesia, and a portion of the alumina by sesquioxide of iron.

These remarks respecting the deduction of formulæ for oxygen salts, apply of course equally to metallic sulphides.

IV. Calculation of the Density of the Vapors of Volatile Bodies, and Application of the Results, as a Means of controlling their Analyses, and determining their Equivalents.

§ 201.

The specific gravity of a compound gas is equal to the sum of the specific gravities of its constituents in one volume.

E.g., 2 volumes of hydrogen gas and 1 volume of oxygen gas give 2 volumes of aqueous vapor. If they gave simply 1 volume of aqueous vapor, the specific gravity of the latter would be equal to the sum total of the specific gravity of the oxygen and double the specific gravity of the hydrogen—viz.,

$$\begin{array}{r}2\times0{\cdot}0693=0{\cdot}1386\\ +1{\cdot}1083\\ \hline =1{\cdot}2469\end{array}$$

But as they give 2 volumes of aqueous vapor, this 1·2469 is distributed between the two volumes; accordingly the specific gravity of the vapor is

$$\frac{1{\cdot}2469}{2}=0{\cdot}62345$$

It will be readily seen that the knowledge of the density of the vapor of a compound supplies an excellent means of controlling the correctness of the relative proportions of the equivalents assumed in a formula.

For instance: from the results of the ultimate analysis of camphor, has been deduced the empirical formula:

$$C_{10}\,H_8\,O.$$

Dumas found the density of the vapor of camphor=5·312. Now, by what means do we find whether this formula is correct with respect to the relative proportions of the equivalents?

Specific gravity of the vapor of carbon	0·831
" " hydrogen gas	0·0693
" " oxygen gas	1·108

$$\begin{array}{r}10\text{ eq. C}=10\text{ volumes}=10\times0{\cdot}831\ =8{\cdot}310\\ 8\text{ eq. H}=16\text{ volumes}=16\times0{\cdot}0693=1{\cdot}109\\ 1\text{ eq. O}=\ 1\text{ volume}\ =\ 1\times1{\cdot}1081=1{\cdot}108\\ \hline 10{\cdot}527\end{array}$$

This sum is almost exactly twice as large as the specific gravity found by direct experiment ($\frac{10{\cdot}527}{2}=5{\cdot}263$); which shows that the relative proportions of the equivalents are correctly given in the empirical formula of camphor. But whether the formula is correct, also, with regard to the absolute number of equivalents, cannot be determined simply from the density of the vapor, because we do not know to how many volumes of camphor vapor 1 equivalent of camphor corresponds. LIEBIG assumes the equivalent of camphor to correspond to 2 volumes, and gives accordingly the formula $C_{10}\ H_8\ O$; whilst DUMAS assumes it to correspond to 4 volumes, and accordingly gives the formula $C_{20}\ H_{16}\ O_2$.

The knowledge of the density of the vapor affords, therefore, in reality, simply a means of controlling the correctness of the analysis, but not of establishing a rational formula; and although it is made to serve sometimes for the latter purpose, yet this can be done only in the case of substances for which we are able to infer from analogy a certain ratio of condensation: thus, for instance, experience proves that 1 equivalent of the hydrates of the volatile organic acids, of alcohols, &c., corresponds to 4 volumes.

In § 200, 2, we have found the rational formula of hydrated benzoic acid to be $C_{14}\ H_6\ O_4$. DUMAS and MITSCHERLICH found the vapor density to be 4·26.

Now nearly the same number is obtained by dividing by 4 the sum total of the gravities of the several constituents contained in 1 equivalent of hydrated benzoic acid, viz.,

14 volumes C = 11·634
12 volumes H = 0·831
4 volumes O = 4·432

$$\frac{16{\cdot}897}{4} = 4{\cdot}224$$

HERMANN KOPP* has called attention to the fact that, if the equivalent of a substance refers to H = 1, and the vapor density of the same to atmospheric air = 1, the division of the equivalent by the vapor density gives the following quotients,

28·88 14·44 7·22

according as the formula corresponds to 4, 2, or 1 volume of vapor:

28·88 corresponds to a condensation to 4 volumes
14·44 " " " 2 "
7·22 " " " 1 volume

KOPP calls these numbers *normal quotients*. If the vapor density is not quite exact, but only approximate (determined by experiment), other numbers are found, but, to be correct, these must come near the normal numbers.

If, therefore, we know the equivalent of a body, we may, with the greatest facility, ascertain whether the determination of the vapor density of the body has given approximately correct results or not.

GAY-LUSSAC found the vapor density of alcohol to be 1·6133; DALTON, 2·1.†

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* Compt. rend. 44, 1347; Chem. Centralbl. 1857, 595.

† Gmelin's Handbook, viii., 199.

Now, which is the correct number?

The equivalent of alcohol, $C_4\,H_6\,O_2$, is 46.

$$\frac{46}{2{\cdot}1}=21{\cdot}9$$

$$\frac{46}{1{\cdot}6133}=28{\cdot}5$$

It is evident that GAY-LUSSAC's number is approximately correct, for the quotient found by it comes very near the normal quotient, 28·88.

Again, if we know the equivalent of a body, and the number of volumes of vapor corresponding to 1 equivalent, we may also, with the same facility, calculate the theoretical vapor density of the body. For instance, the equivalent of hydrated benzoic acid is 122. The division of this number by 28·88 gives 4·224 as vapor density, which is the same as that found by actual experiment.

And, lastly, if we know approximately (*i.e.* by experiment) the vapor density of a body, and also the ratio of condensation, we may, with the aid of these quotients, approximately calculate the equivalent of the body.

E.g. The vapor density of acetic ether has been found = 3·112. The multiplication of this number by 28·88 gives 89·87 as the equivalent of acetic ether, which comes near the actual equivalent, 88.

Having thus shown how the knowledge of the vapor density of a body is turned to account as a means of controlling the results of an ultimate analysis of the same, we will now proceed to show how the vapor density is calculated from the data obtained as described in § 191, A and B.

A. We will take as an illustration DUMAS' estimation of the specific gravity of the vapor of camphor.

The results of the process were as follows:—

Temperature of the air	13·5°
Barometer	742 mm.
Temperature of the bath at the moment of sealing the globe	244°
Increase of the weight of the globe	0·708 grm.
Volume of mercury entering the globe	295 c.c.
Residual air	0

Now, to find the vapor density, we have to determine,

1. The weight of the air which the globe holds (as a necessary step to the determination of 2).
2. The weight of the camphor vapor which the globe holds.
3. The volume to which the camphor vapor corresponds, at 0° and 760 mm.

The solution of these questions is quite simple; and if the calculation, notwithstanding, appears somewhat complicated, this is merely owing to certain reductions and corrections which are required.

1. *The weight of the air in the globe.*

The globe holds 295 c. c., as we see by the volume of mercury required to fill it.

This sum is almost exactly twice … ad 742 mm.,
by direct experiment ($\frac{10\cdot527}{2}=5\cdot263$); … ons of § 195, as
portions of the equivalents are cor
of camphor. But whether the f
the absolute number of equivale
the density of the vapor, becau … and 760 mm.)
of camphor vapor 1 equivalent
the equivalent of camphor to
ingly the formula $C_{10}\,H_8\,O$;
4 volumes, and accordingly … (at 0° and 760 mm.)

The knowledge of the d
simply a means of contr … m. weighs 0·00129366 grm.; 274
establishing a rational f
times for the latter pu … 4=0·35446 grm.
stances for w
condensation
the hydrat
to 4 volu

In § 20 … periment we tared the globe+the air
acid to 1 … hed the globe+the vapor (but without
sity to … actual weight of the vapor, it is not
… from the weight of the globe filled with

Now … (*glass*+*air*) is not=*vapor*; but we have
total … place, the weight of the air from the tare,
lent … air to the increase of the weight of the
…:—

ir in the globe . =0·35446 grm.
weight of globe . =0·70800 grm.

vapor is accordingly =1·06246 grm.

to which this Weight of 1·06246 *grm. of Vapor cor-*
760 *mm.*

Hi … the above-given data that this weight corresponds to
of a … , and 742 mm. Before we can proceed to reduce this
mos … g to the directions of § 195, the following corrections
giv

a … the mercurial thermometer correspond, according to the
of MAGNUS, to 239° of the air thermometer (see Table

… ing to DULONG and PETIT, glass expands (commencing at
… its volume for each degree C. The volume of the globe at
… of sealing was accordingly—

$$295+\frac{295\times239}{35000}=297 \text{ c. c.}$$

… now proceed to reduce this volume to 0° and 760 mm. we find
… proportion,

$$760 : 742 :: 297 : x$$

$$x \ (i.e., \text{ c. c. of vapor at 760 mm. and } 239°)=290;$$

the equation,

$$\frac{290}{1+(239\times 0\cdot 00366)}=x$$

x (*i.e.* c. c. of vapor at 760 mm. and 0°)$=154\cdot 6$.

154·6 c. c. of camphor vapor at 0° and 760 mm., weigh accordingly 1·06246 grm.

1 litre (1000 c. c.) weighs consequently 6·87231 grm.; since

$$154\cdot 6 : 1\cdot 06246 :: 1000 : 6\cdot 87231.$$

Now 1 litre of air at 0° and 760 mm. weighs 1·29366 grm.

The specific gravity of the camphor vapor consequently = 5·312; since

$$1\cdot 29366 : 6\cdot 87231 :: 1 : 5\cdot 312.$$

B. We will here take an imaginary determination of the vapor density of ether as our example.

Bulb + ether	=0·3445 grm.
" empty	=0·2040 grm.
Weight of ether	=0·1405 grm.

Temperature of the glycerine solution in the outer cylinder	100°
Sp. gr. of the same solution at 100°	1
Barometer	752 mm.
Difference between the height of the mercury in the outer and inner cylinders	50 mm.
Height of the column of mercury in the outer cylinder	60 mm.
Inside height of the outer cylinder	400 mm.
Volume of the vapor as found from the tube's table	60 c. c.

The glycerine solution being $400-60=340$ mm. high and having a specific gravity of 1, corresponds to a column of mercury of 25 mm. The vapor consequently is under the pressure of $752+25-50=727$ mm. 60 c. c. of ether vapor at 100° and 727 mm. consequently weigh 0·1405. We have now to calculate the weight of 60 c. c. of air under the same circumstances.

1000 c. c. air of 0° and 760 mm. weigh 1·29366 grm. Heated to 100° they become 1366·5 c. c. (comp. § 195, α), and with the pressure reduced to 727 mm. these expand again to 1428·5 c. c. (comp. § 195, β). But the air still weighs the same, viz., 1·29366 grm. $\therefore$ 1428·5 c. c. weighing 1·29366, 60 c. c. weigh, under the same circumstances, 0·05433 grm.;

hence the sp. gr. of ether vapor $=\frac{0\cdot 1405}{0\cdot 05433}=2\cdot 586$

PART II.

SPECIAL PART.

1. ANALYSIS OF FRESH WATER (SPRING-WATER, RIVER-WATER, &c.)[*]

§ 202.

THE analysis of the several kinds of fresh water is *usually* restricted to the quantitative estimation of the following substances:—

a. Bases: Soda, lime, magnesia.

b. Acids: Sulphuric acid, nitric acid, silicic acid, carbonic acid, chlorine.

c. Mechanically suspended Matters: Clay, &c.

We confine ourselves, therefore, here to the estimation of these bodies.

I. *The Water is clear.*

1. *Determination of the Chlorine.*—This may be effected, either, *a*, in the gravimetric, or, *b*, in the volumetric way.

a. Gravimetrically.

Take 500—1000 grm. or c. c.[†] Acidify with nitric acid, and precipitate with nitrate of silver. Filter when the precipitate has *completely* subsided (§ 141, I., *a*). If the quantity of the chlorine is so inconsiderable that the solution of nitrate of silver produces only a slight turbidity, evaporate a larger portion of the water to $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{6}$, &c., of its bulk, filter, wash the precipitate, and treat the filtrate as directed.

b. Volumetrically.

Evaporate 1000 grm. or c. c. to a small bulk, and determine the chlorine in the residual fluid, without previous filtration, by solution of nitrate of silver, with addition of chromate of potassa (§ 141, I., *b*, α).

2. *Determination of the Sulphuric Acid.*—Take 1000 grm. or c. c. Acidify with hydrochloric acid and mix with chloride of barium. Filter after the precipitate has *completely* subsided (§ 132, I., 1). If the quantity of the sulphuric acid is very inconsiderable, evaporate the acidified water to $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{6}$, &c., of the bulk, before adding the chloride of barium.

3. *Determination of Nitric Acid.*—If, on testing the residue on evaporation of a water for nitric acid, such a strong reaction is obtained that the presence of a determinable quantity of the acid may be inferred, evaporate 1000 or 2000 c. c. of the water in a porcelain dish, wash the residue into a flask (if any carbonate of lime, &c., remains sticking to the dish, it may be disregarded, as all nitrates are soluble), evaporate in the flask still further, if necessary, and in the small quantity of residual fluid determine the nitric acid according to § 149, *d*, α, or β. The former method is less suitable if the residue on evaporation contains organic matter. If the latter method is employed, the evaporated water

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[*] Compare Qualitative Analysis, p. 262, et seq. See a paper recently read before the Chemical Society by Dr. Miller—the Society's Journal (2), iii., 117, et seq.; also, Frankland, idem (2), iv., 239, and vi., 77; and Wanklyn, Chapman, and Smith, idem vi., 152.

[†] As the specific gravity of fresh water differs but little from that of pure water, the several quantities of water may safely be measured instead of weighed. The calculation is facilitated by taking a round number of c. c.

must first be heated with potash solution till no more alkaline vapors escape.

4. *Determination of the Silicic Acid, Lime, and Magnesia.*

Evaporate 1000 grm. or c. c. to dryness—after addition of some hydrochloric acid—preferably in a platinum dish, treat the residue with hydrochloric acid and water, filter off the separated silicic acid, and treat the latter as directed § 140 II., *a*. Estimate the lime and magnesia in the filtrate as directed § 154, 6, *a* (**29**).

5. *Determination of the total Residue and of the Soda.*

a. Evaporate 1000 grm. or c. c. of the water, with proper care, to dryness in a weighed platinum dish, first over a lamp, finally on the water-bath. Expose the residue, in the air-bath, to a temperature of about 180°, until no further diminution of weight takes place. This gives the *total amount of the salts.*

b. Treat the residue with water, and add, cautiously, pure dilute sulphuric acid in moderate excess; cover the vessel during this operation with a dish, to avoid loss from spirting; then place on the water-bath, without removing the cover. After ten minutes, rinse the cover by means of a washing bottle, evaporate the contents of the dish to dryness, expel the free sulphuric acid, ignite the residue, in the last stage with addition of some carbonate of ammonia (§ 97, 1), and weigh. The residue consists of sulphate of soda, sulphate of lime, sulphate of magnesia, and some separated silicic acid. It must not redden moist litmus paper. The quantity of the sulphate of soda in the residue is now found by subtracting from the weight of the latter the known weight of the silicic acid and the weight of the sulphate of lime and sulphate of magnesia calculated from the quantities of these earths found in 4.

6. *Direct Estimation of the Soda.*

The soda may also be determined in the direct way, with comparative expedition, by the following method:—

Evaporate 1250 grm. or c. c. of the water, in a dish, to about $\frac{1}{6}$, and then add 2—3 c. c. of thin pure milk of lime, so as to impart a strongly alkaline reaction to the fluid; heat for some time longer, then wash the contents of the dish into a quarter-litre flask. (It is not necessary to rinse every particle of the precipitate into the flask; but the whole of the fluid must be transferred to it, and the particles of the precipitate adhering to the dish well washed, and the washings also added to the flask.) Allow the contents to cool, dilute to the mark, shake, allow to deposit, filter through a dry filter, measure off 200 c. c. of the filtrate, corresponding to 1000 grm. of the water, transfer to a quarter-litre flask, mix with carbonate of ammonia and some oxalate of ammonia, add water up to the mark, shake, allow to deposit, filter through a dry filter, measure off 200 c. c., corresponding to 800 grm. of the water, add some chloride of ammonium,[*] evaporate, ignite, and weigh the residual chloride of sodium as directed § 98, 2.[†]

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[*] To convert the still remaining sulphate of soda, on ignition, into chloride of sodium.

[†] This process, which entirely dispenses with washing, presents one source of error—viz., the space occupied by the precipitates is not taken into account. The error resulting from this is, however, so trifling, that it may safely be disregarded, as the excess of weight amounts to $\frac{1}{500}$ at the most.

7. Calculate the numbers found in 1—6 to 1000 parts of water, and determine from the data obtained the amount of *carbonic acid* in combination, as follows:—

Add together the quantities of sulphuric acid corresponding to the bases found, and subtract from the sum, first, the amount of sulphuric acid precipitated from the water by chloride of barium (2), secondly, the amount corresponding to the nitric acid found, and thirdly, the amount corresponding to the chlorine found (for 1 eq. Cl, 1 eq. SO_3); the remainder is equivalent to the carbonic acid combined with the bases in the form of *neutral* carbonates. 40 parts of sulphuric acid remaining after subtracting the quantities just stated, correspond accordingly to 22 parts of carbonic acid.

If, by way of control, you wish to determine the combined carbonic acid in the direct way, evaporate 1000 grm. or c. c. of the water, in a flask, to a small bulk; add tincture of cochineal, then standard nitric acid, and proceed as directed p.

8. *Control.*

If the quantities of the soda, lime, magnesia, sulphuric acid, nitric acid, silicic acid, carbonic acid, and chlorine are added together, and an amount of oxygen corresponding to the chlorine (since this latter is combined with metal and not with oxide) is subtracted from the sum, the remainder must nearly correspond to the total amount of the salts found in 5, *a*. *Perfect* correspondence cannot be expected, since, 1, upon the evaporation of the water chloride of magnesium is partially decomposed, and converted into a basic salt; 2, the silicic acid expels some carbonic acid; and 3, it being difficult to free carbonate of magnesia from water without incurring loss of carbonic acid, the residue remaining upon the evaporation of the water contains the carbonate of magnesia as a basic salt, whereas, in our calculation, we have assumed the quantity of carbonic acid corresponding to the neutral salt.

9. *Determination of the free Carbonic Acid.*

In the case of well-water this may be conveniently executed by the process described § 139, β (p. 286). We here obtain the carbonic acid which is contained in the water over and above the quantity corresponding to the monocarbonates, or in other words, the carbonic acid which is free and which is combined with the carbonates to bicarbonates.

10. *Determination of the Organic Matter.*

Many well-waters contain so much organic matter as to be quite yellow, others contain traces, and many again may be said to be free from such substances. The exact estimation of organic matter is by no means an easy task, and the method usually adopted—viz., ignition of the residue of the water dried at 180°, treatment with carbonate of ammonia, gentle ignition again, and calculation of the organic matter from the loss of weight—yields merely an approximate result, since we can never be sure as to the condition of the carbonate of magnesia in the residue dried at 180° and in the same after ignition, and since the silicic acid expels some carbonic acid, which is not taken up again on treatment with carbonate of ammonia, &c. However, it is generally a matter of importance, in regard to the application of a water, to know the quantity of organic matter present, hence we have lately had recourse to the permanganate of potassa, and sought to determine the organic matter at least comparatively from the quantity of the oxidizing agent reduced by a definite amount of water. FORCHHAMMER* heats a certain quantity of the water to boiling, runs in a dilute solution of permanganate from a burette, till a faint but permanent redness occurs, he then allows to cool, and to a like quantity of pure distilled water adds permanganate from the same burette till a similar coloration is formed; lastly, he finds from the difference the quantity of permanganate reduced by the substances contained in the water. EM. MONNIER† uses a solution of 1 grm. permanganate of potassa in 1 litre of distilled water, purified by rectification over some permanganate of potassa. He warms 500 c. c. of the water to 70°, adds 1 c. c. pure sulphuric acid, and then the standard solution of permanganate to incipient coloration, and finally, deducting from the quantity employed the quantity necessary to impart the same coloration to 500 c. c. of purified distilled water, acidulated and heated as above, he obtains the quantity of permanganate which has been reduced by the substances present in the water tested.

Comparative experiments of this kind are often of value; but they do not provide us with a numerical expression for the amount of organic substances present, since waters contain sometimes other bodies, especially nitrites, sulphuretted hydrogen, and salts of protoxide of iron, which have the property of reducing permanganate of potassa, and since again organic substances decompose various quantities of this salt, according to their nature.

II. *The water is not clear.*

Fill a large flask of known capacity with the water, close with a glass stopper, and allow the flask to stand in the cold until the suspended matter is deposited; draw off the clear water with a siphon as far as practicable, filter the bottoms, dry or ignite the contents of the filter, and weigh. Treat the clear water as directed in I.

Respecting the calculation of the analysis, I remark simply that the results are *usually*‡ arranged upon the following principles:—

The *chlorine* is combined with sodium; if there is an excess, this is combined with calcium. If, on the other hand, there remains an excess of soda, this is combined with sulphuric acid. The *sulphuric acid*, or the remainder of the sulphuric acid, as the case may be, is combined with lime. The *nitric acid* is, as a rule, to be combined with lime. The *silicic acid* is put down in the free state, the remainder of the *lime* and the *magnesia* as carbonates, either neutral or acid, according to circumstances.

It must always be borne in mind that the results of the qualitative analysis may render another arrangement of the acids and bases necessary. For instance, if the evaporated water reacts strongly alkaline, carbonate of soda is present, generally in company with sulphate of soda and chloride of sodium, occasionally also with nitrate of soda.

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* Institut. 1849, 383; Jahresber. von v. Liebig u. Kopp. 1849, 603.

† Compt. rend. 50, 1084; Dingler's polyt. Journ. 157, 132.

‡ A certain latitude is here allowed to the analyst's discretion.

The lime and magnesia are then to be entirely combined with carbonic acid.

In the report, the quantities are represented in parts per 1000 (or 1000,000), and also in grains per gallon.

For technical purposes, it is sometimes sufficient to estimate the *hardness* of the water (the relative amount of lime and magnesia in it) by means of a standard solution of soap. A detailed description of this method, which was first employed by CLARK, may be found in BOLLEY & PAUL's Handbook of Technical Analysis. See also SUTTON's Volumetric Analysis.

2. ACIDIMETRY.

A. ESTIMATION BY SPECIFIC GRAVITY.

§ 203.

Tables, based upon the results of exact experiments, have been drawn up, expressing in numbers the relation between the specific gravity of the aqueous solution of an acid, and the amount of real acid contained in it. Therefore, to know the amount of real acid contained in an aqueous solution of an acid, it suffices, in many cases, simply to determine its specific gravity. Of course the acids must, in that case, be free, or at least nearly free from admixtures of other substances dissolved in them. Now, as most common acids are volatile (sulphuric acid, hydrochloric acid, nitric acid, acetic acid), any non-volatile admixture may be readily detected by evaporating a sample of the acid in a small platinum or porcelain dish.

The determination of the specific gravity is effected either by comparing the weight of equal volumes of water and acid,* or by means of a good hydrometer. The estimations must, of course, be made at the temperature to which the Tables refer.

The Tables on pages 488—491 give the relations between the specific gravity and the strength for sulphuric acid, hydrochloric acid, nitric acid, and acetic acid.

In all cases in which the determination of the specific gravity fails to attain the end in view, or which demand particular accuracy, the following method is employed.

B. ESTIMATION BY SATURATION WITH AN ALKALINE FLUID OF KNOWN STRENGTH.†

§ 204.

This method requires :—

A dilute acid of known strength.
An alkaline fluid of known strength.

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* See Greville Williams' Chemical Manipulation.

† According to Nicholson and Price (Chem. Gaz., 1856, p. 30) the common method of acidimetry is not suited for determining free acetic acid, on account of the alkaline reaction of neutral acetate of soda; however, Otto (Annal. d. Chem. u. Pharm. 102, 69) has clearly demonstrated that the error arising from this is so inconsiderable that it may safely be disregarded.

TABLE I.

Showing the percentages of hydrated and anhydrous acid corresponding to various specific gravities of aqueous *Sulphuric Acid* by BINEAU; calculated for 15°, by OTTO.

Specific gravity.	Percentage of hydrated acid.	Percentage of anhydrous acid.	Specific gravity.	Percentage of hydrated acid.	Percentage of anhydrous acid.
1·8426	100	81·63	1·398	50	40·81
1·842	99	80·81	1·3886	49	40·00
1·8406	98	80·00	1·379	48	39·18
1·840	97	79·18	1·370	47	38·36
1·8384	96	78·36	1·361	46	37·55
1·8376	95	77·55	1·351	45	36·73
1·8356	94	76·73	1·342	44	35·82
1·834	93	75·91	1·333	43	35·10
1·831	92	75·10	1·324	42	34·28
1·827	91	74·28	1·315	41	33·47
1·822	90	73·47	1.306	40	32·65
1·816	89	72·65	1·2976	39	31·83
1·809	88	71·83	1·289	38	31·02
1·802	87	71·02	1·281	37	30·20
1·794	86	70·10	1·272	36	29·38
1·786	85	69·38	1·264	35	28·57
1·777	84	68·57	1·256	34	27·75
1·767	83	67·75	1·2476	33	26·94
1·756	82	66·94	1·239	32	26·12
1·745	81	66·12	1·231	31	25·30
1·734	80	65·30	1·223	30	24·49
1·722	79	64·48	1·215	29	23·67
1·710	78	63·67	1·2066	28	22·85
1·698	77	62·85	1·198	27	22·03
1·686	76	62·04	1·190	26	21·22
1·675	75	61·22	1·182	25	20·40
1·663	74	60·40	1·174	24	19·58
1·651	73	59·59	1·167	23	18·77
1·639	72	58·77	1·159	22	17·95
1·627	71	57·95	1·1516	21	17·14
1.615	70	57·14	1·144	20	16·32
1·604	69	56·32	1·136	19	15·51
1·592	68	55·59	1·129	18	14·69
1·580	67	54·69	1·121	17	13·87
1·568	66	53·87	1·1136	16	13·06
1·557	65	53·05	1·106	15	12·24
1·545	64	52·24	1·098	14	11·42
1·534	63	51·42	1·091	13	10·61
1·523	62	50·61	1·083	12	9·79
1·512	61	49·79	1·0756	11	8·98
1·501	60	48·98	1·068	10	8·16
1·490	59	48·16	1·061	9	7·34
1·480	58	47·34	1·0536	8	6·53
1·469	57	46.53	1·0464	7	5·71
1·4586	56	45·71	1·039	6	4·89
1·448	55	44·89	1·032	5	4·08
1·438	54	44·07	1·0256	4	3·26
1·428	53	43·26	1·019	3	2·445
1·418	52	42·45	1·013	2	1·63
1·408	51	41·63	1·0064	1	0·816

TABLE II.

Showing the percentages of anhydrous acid corresponding to various specific gravities of aqueous *Hydrochloric Acid*, by Ure. Temperature 15°.

Specific gravity.	Percentage of hydrochloric acid gas.	Specific gravity.	Percentage of hydrochloric acid gas.
1·2000	40·777	1·1000	20·388
1·1982	40·369	1·0980	19·980
1·1964	39·961	1·0960	19·572
1·1946	39·554	1·0939	19·165
1·1928	39·146	1·0919	18·757
1·1910	38·738	1·0899	18·349
1·1893	38·330	1·0879	17·941
1·1875	37·923	1·0859	17·534
1·1857	37·516	1·0838	17·126
1·1846	37·108	1·0818	16·718
1·1822	36·700	1·0798	16·310
1·1802	36·292	1·0778	15·902
1·1782	35·884	1·0758	15·494
1·1762	35·476	1·0738	15·087
1·1741	35·068	1·0718	14·679
1·1721	34·660	1·0697	14·271
1·1701	34·252	1·0677	13·863
1·1681	33·845	1·0657	13·456
1·1661	33·437	1·0637	13·049
1·1641	33·029	1·0617	12·641
1·1620	32·621	1·0597	12·233
1·1599	32·213	1·0577	11·825
1·1578	31·805	1·0557	11·418
1·1557	31·398	1·0537	11·010
1·1537	30·990	1·0517	10·602
1·1515	30·582	1·0497	10·194
1·1494	30·174	1·0477	9·786
1·1473	29·767	1·0457	9·379
1·1452	29·359	1·0437	8·971
1·1431	28·951	1·0417	8·563
1·1410	28·544	1·0397	8·155
1·1389	28·136	1·0377	7·747
1·1369	27·728	1·0357	7·340
1·1349	27·321	1·0337	6·932
1·1328	26·913	1·0318	6·524
1·1308	26·505	1·0298	6·116
1·1287	26·098	1·0279	5·709
1·1267	25·690	1·0259	5·301
1·1247	25·282	1·0239	4·893
1·1226	24·874	1·0220	4·486
1·1206	24·466	1·0200	4·078
1·1185	24·058	1·0180	3·670
1·1164	23·650	1·0160	3·262
1·1143	23·242	1·0140	2·854
1·1123	22·834	1·0120	2·447
1·1102	22·426	1·0100	2·039
1·1082	22·019	1·0080	1·631
1·1061	21·611	1·0060	1·124
1·1041	21·203	1·0040	0·816
1·1020	20·796	1·0020	0·408

Showing [illegible] corresponding to various [illegible] by URE. Temperature [illegible]

Specific gravity.	Percentage of anhydrous acid.	Specific gravity.	Percentage of anhydrous acid.
[illegible]	39·8	1·140	19·9
[illegible]	39·0	1·134	19·1
[illegible]	38·3	1·129	18·3
[illegible]	37·5	1·123	17·5
[illegible]	36·7	1·117	16·7
[illegible]	35·9	1·111	15·9
[illegible]	35·1	1·105	15·1
[illegible]	34·3	1·099	14·3
[illegible]	33·5	1·093	13·5
[illegible]	32·7	1·088	12·7
[illegible]	31·9	1·082	11·9
[illegible]	31·1	1·076	11·2
[illegible]	30·3	1·071	10·4
[illegible]	29·5	1·065	9·6
[illegible]	28·7	1·059	8·8
[illegible]	27·9	1·054	8·0
[illegible]	27·1	1·048	7·2
[illegible]	26·3	1·043	6·4
[illegible]	25·5	1·037	5·6
[illegible]	24·7	1·032	4·8
[illegible]	23·9	1·027	4·0
[illegible]	23·1	1·021	3·2
[illegible]	22·3	1·016	2·4
[illegible]	21·5	1·011	1·6
[illegible]	20·7	1·005	0·8

[illegible] to contain in 1000 c. c. the exact [illegible] of the acid, accordingly, 40 grm. [illegible] 36 oxalic acid, &c. Acids of [illegible] equal volumes of them have the [illegible] Their use is convenient for techni- [illegible] more dilute acids, either deci- [illegible] standard. As the first step in the [illegible] of convenient strength for ordi- [illegible] oil of vitriol with water to the

[illegible] commercial caustic potash; this is [illegible] given volume, e. g. 5 c. c., neutral- [illegible] is determined by a few rough

[illegible] heated to boiling in a flask, and a [illegible] decompose any carbonate of pot- [illegible] a few minutes and, finally, the ley is [illegible] collected in the bottle from [illegible]

TABLE IV.

Showing the percentages of hydrated acid corresponding to various specific gravities of aqueous *Acetic Acid*, by MOHR.

Specific gravity.	Percentage of hydrated acid.	Specific gravity.	Percentage of hydrated acid.	Specific gravity.	Percentage of hydrated acid.	Specific gravity.	Percentage of hydrated acid.	Specific gravity.	Percentage of hydrated acid.
1·0635	100	1·0735	80	1·067	60	1·051	40	1·027	20
1·0655	99	1·0735	79	1·066	59	1·050	39	1·026	19
1·0670	98	1·0732	78	1·066	58	1·049	38	1·025	18
1·0680	97	1·0732	77	1·065	57	1·048	37	1·024	17
1·0690	96	1·0730	76	1·064	56	1·047	36	1·023	16
1·0700	95	1·0720	75	1·064	55	1·046	35	1·022	15
1·0706	94	1·0720	74	1·063	54	1·045	34	1·020	14
1·0708	93	1·0720	73	1·063	53	1·044	33	1·018	13
1·0716	92	1·0710	72	1·062	52	1·042	32	1·017	12
1·0721	91	1·0710	71	1·061	51	1·041	31	1·016	11
1·0730	90	1·0700	70	1·060	50	1·040	30	1·015	10
1·0730	89	1·0700	69	1·059	49	1·039	29	2·013	9
1·0730	88	1·0700	68	1·058	48	1·038	28	1·012	8
1·0730	87	1·0690	67	1·056	47	1·036	27	1·010	7
1·0730	86	1·0690	66	1·055	46	1·035	26	1·008	6
1·0730	85	1·0680	65	1·055	45	1·034	25	1·007	5
1·0730	84	1·0680	64	1·054	44	1·033	24	1·005	4
1·0730	83	1·0680	63	1·053	43	1·032	23	1·004	3
1·0730	82	1·0670	62	1·052	42	1·031	22	1·002	2
1·0732	81	1·0670	61	1·051	41	1·029	21	1·001	1

which it is to be used. Care should be taken to bring upon the filter some of the excess of lime that is suspended in the liquid, so that the latter may acquire no carbonic acid from the air. This clear liquid thus obtained is a potash-lye containing lime in solution. If exposed to the air, the carbonic acid that is absorbed separates as carbonate of lime, leaving the liquid perfectly caustic.

It now remains to determine with the greatest accuracy, 1st, the volume of alkali which neutralizes a cubic centimetre of the acid, and, 2d, the amount of SO_3 contained in a cubic centimetre of the latter.

As a means of recognizing the point of neutralization, tincture of cochineal possesses great advantages over solution of litmus. The knowledge of this fact is due to LUCKOW, who has detailed its application in *Jour. für Pract. Chem.*, lxxxiv., p. 424. Tincture of cochineal is prepared by digesting and frequently agitating three grammes of pulverized cochineal in a mixture of 50 cubic centimetres of strong alcohol with 200 c. c. of distilled water, at ordinary temperatures, for a day or two. The solution is decanted, or filtered through Swedish paper.

The tincture thus prepared has a deep ruby-red color. On gradually diluting with pure water (free from ammonia), the color becomes orange and finally yellowish-orange. Alkalies and alkali-earths as well as their carbonates change the color to a carmine or violet-carmine. Solutions of strong acid and acid salts make it orange or yellowish-orange.

To determine the volumetric relation of the alkali and acid, a given volume of the latter, e. g. 20 c. c., is measured off into a wide-mouthed flask, ten drops of cochineal-tincture, and about 150 c. c. of water are added—the alkali is now allowed to flow in from a burette, until the yellowish liquid in the flask, suddenly, and by a single drop, acquires a violet-carmine tinge.

In nicer determinations, it is important to bring the liquid each time to a given volume, by adding water after the neutralization is nearly finished. For this purpose, two or more flasks of equal capacity are selected, and on the outside of each a strip of paper is gummed to indicate the level of the proper amount of liquid, e. g. 200 c. c. The same amount of coloring matter being thus always diffused in the same volume of the same water, the errors of varying dilution and varying amount of ammonia (which is rarely absent from distilled water) are avoided. The contents of one flask, in which the neutralization has been satisfactorily effected, may be kept as a standard of color for the succeeding trials, as the tint remains constant for hours, being unaffected by the absorption of carbonic acid. The greatest convenience and accuracy of measurement are obtained by using burettes provided with ERDMANN's swimmer (See p. 30.)

When three or four accordant results have been obtained, the average is taken as expressing the relative strength of the acid and alkali.

To ascertain the absolute standard, weigh off in a small platinum crucible about 0·8 grm. of pure carbonate of soda, ignite to dull redness, cool and weigh accurately: bring the crucible with its contents into one of the wide-mouthed flasks and let flow from the burette a slight excess, e. g. 50 c. c., of standard acid. The solution of carbonate of soda is facilitated by warming, and, finally, the contents of the flask are gently boiled for several minutes to expel carbonic acid. The solution is now allowed to become *perfectly cold*, then add ten drops of cochineal and lastly the standard alkali to neutralization, diluting to the proper volume.

To illustrate the accuracy of the process and the calculations employed, the following actual data may be useful. The normal acid was made by diluting 50 c. c. of oil-of-vitriol to the volume of ten litres and had half the strength above recommended. The alkali was from a stock on hand and more dilute than necessary.

Relation of acid to alkali.

Exp. I.,	20 c. c. SO_3=32·8 c. c. KO, or 1 : 1·64
Exp. II.,	20 c. c. SO_3=32·8 c. c. KO, or 1 : 1·64
Exp. III.,	40 c. c. SO_3=65·7 c. c. KO, or 1 : 1·6425

We have accordingly:

1 c. c. SO_3=1·64 c. c. KO and 1 c. c. KO=0·60976 c. c. SO_3

Absolute strength of acid and alkali.

Exp. I. 0·4177 grm. of carbonate of soda were treated with 44·2 of SO_3. To neutralize the excess of the acid were required 3·8 c. c., KO, which correspond to 2·32 c. c. SO_3(3·8×0·60976). Deducting this from the total amount of acid (44·2—2·32) we have 41·88 c. c. of acid, equivalent to the carbonate of soda taken.

$$41\cdot88 \text{ c. c. solution of } SO_3 = 0\cdot4197 \text{ grm. NaO } CO_2.$$

Exp. II. 0·4126 grm. NaO Co_2 treated with 44 c. c. SO_3 required 4·28 c. c. KO. 4·28 × 0·60976 = 2·61 c. c. SO_3. 44 − 2·61 = 41·39 c. c. SO_3.

$$41\cdot39 \text{ c. c. solution of } SO_3 = 0\cdot4126 \text{ grms. NaO } CO_2.$$

It is convenient to calculate how much acid corresponds to 53 decigrammes of carbonate of soda, since the relation of any other substance to the acid is then obtained by substituting its equivalent number for 53 (the equivalent of NaO CO_2), in the following equation, thus:

$$\begin{array}{lccc} & \overbrace{}^{\text{grms. NaO CO}_2} & & \overbrace{}^{\text{c. c. SO}_3} \\ \text{I.} & 0\cdot4177 : 0\cdot53 & :: & 41\cdot88 : 53\cdot14 \\ \text{II.} & 0\cdot4126 : 0\cdot53 & :: & 41\cdot39 : 53\cdot17 \end{array}$$

Accordingly 0·53 grm. NaO CO_2 neutralize 53·155 c. c. SO_3.

If, for example, the solutions are employed for nitrogen estimations (§ 185), we learn how much nitrogen corresponds to 1 c. c. of acid, by the following proportion:

$$\overbrace{53\cdot155 : 1}^{\text{c. c. SO}_3} \quad :: \quad \overbrace{0\cdot140 : 0\cdot002634}^{\text{grm. N.}}$$

We may then write on the label of the acid bottle the following data for calculation.

1 c. c. KO = 0·60976 c. c. SO_3.
1 c. c. SO_3 = 1·64 c. c. KO.
1 c. c. SO_3 = 0·002634 grm. N.

According to Luckow, cochineal is quite indifferent to carbonic and sulphydric acids, carminic acid being stronger than these. This is practically true for solutions of considerable strength. *Hence a Normal Alkali for technical analysis may be prepared by simply dissolving 53 grms. of pure and anhydrous carbonate of soda in a litre of water.* To make a *normal acid* mix 1050 c. c. of water with 60 grm. of concentrated sulphuric acid, let cool and ascertain as just described how many c. c. of this acid neutralize 50 c. c. of normal carbonate of soda. Suppose 48·6 c. c. are required, then 50 − 48·6 = 1·4 c.c. of water must be added to every 48·6 c. c. of acid to make it normal. For a litre of normal acid 48·6 × 20 972 c. c. of this acid and 28 c.c. of water should be mixed. As it is difficult to do this with accuracy, we ascertain how much water is needed to bring 1000 c. c. of the acid to the normal strength.

$$972 : 1000 :: 28 : x$$
$$x = 28\cdot8$$

Fill, therefore, a flask *holding* a litre to the mark with the acid, add from a burette 28·8 c. c. of water and mix. Test finally the acid against the alkali to be certain that equal volumes neutralize each other.

Decinormal solutions may be prepared by diluting 100 c. c. of the normal solutions to a litre, or taking 5·3 grms. of carbonate of soda as the starting point. In the neutralization it is not needful to expel carbonic acid by boiling. The influence of the latter is however at once seen when a caustic and carbonated alkali are operated with side by side. In case of the former, the point of neutralization (or rather of supersaturation), is shown by a prompt and decisive change from a tint in which orange predominates, to one in which this disappears and violet is most marked. In presence of carbonic acid the change is somewhat gradual, and though a red color is produced it is modified by an orange tint, even in presence of a large excess of alkali. Hence, it is to be recommended, especially in nice investigations, to employ a caustic alkali. A trifle less of it will be found needful to neutralize a given volume of acid, than is required of a carbonated solution, and no doubt will exist as to the point of saturation.*

This indifference towards carbonic acid is a great advantage in nice analyses, in that the time consumed for effecting neutralization is without influence on the result. When litmus is used and the point of neutralization is reached, a short exposure to the air suffices to redden the liquid again. If the operator is obliged to proceed slowly, he will require somewhat more alkali than when he operates rapidly; a portion of it being neutralized by atmospheric carbonic acid. With cochineal, the result is independent of the small amount of carbonic acid that can come from the air. The permanence of the color also allows several titrations to be compared directly together.

Another advantage of cochineal is, that its solution, prepared as above described, may be preserved indefinitely in closed vessels, without decolorization or alteration.

b. The Actual Analysis.—It is only necessary to weigh or measure off a quantity of the acid to be examined and ascertain how much standard alkali is required for its neutralization, as has been detailed. The selection of the alkaline fluid depends, of course, entirely upon the quantity of acid to be neutralized. The neutralization of the weighed or measured acid fluid should take about 15—30 c. c.

In scientific investigations, I recommend the weighing of indeterminate quantities of the acid fluid, as the weighing of definite quantities on a chemical balance is troublesome, and the trouble of calculation is not worth mentioning. Suppose, for instance, you have weighed off 4·5 grm. of a dilute acetic acid, and used 25 c. c. normal solution of soda to neutralize this, you find by the proportion,

$$1000 : 25 :: 60 \text{ (eq. } C_4H_4O_4) : x;\ x = 1{\cdot}5,$$

that 1·5 grm. of hydrated acetic acid are contained in the weighed quantity of the dilute acid; and another proportion, viz.,

$$4{\cdot}5 : 1{\cdot}5 :: 100 : x;\ x = 33{\cdot}33$$

gives the percentage of hydrated acetic acid contained in the analyzed fluid. Or, the calculation may also be made as follows:—

4·5 grm. of the acetic acid examined having required 25 c. c. of normal solution of soda for neutralization, how much would 6 grm. (*i. e.* the weight of $\frac{1}{10}$ eq. grm. hydrated acetic acid) require?

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* Collier has made some experiments with a sulphuric acid containing 25 c. c. oil of vitriol to the litre, and a solution of carbonate of soda, and he found, when CO_2 was expelled by boiling, that 10 c. c. SO_3=7·66 and 7·67 c. c. of $NaO\ CO_2$; when CO_2 was not expelled, 10 c. c. SO_3=7·68 and 7·7. These results are as good as identical. In standarding the much weaker acid above mentioned, he obtained for it a value slightly too low when CO_2 was not removed. 0·53 grm. $NaO\ CO_2$ required in this case but 53·05 c. c. SO_3, instead of 53·155 as in the other instances. This is a very slight difference and not appreciable perhaps with ordinary burettes, but it is a constant and perceptible difference. What is of more importance is the uncertainty as to the point of neutralization.

$$4{\cdot}5 : 6 :: 25 : x;\ x = 33{\cdot}33$$

It is evident that in this case the number of c. c. found as x expresses the percentage of hydrated acetic acid, since 100 c. c. of normal solution of soda correspond to $\frac{1}{10}$ eq. grm. pure hydrated acid, *i. e.* acetic acid of 100 per cent.

In technical analyses it is more convenient if the number of c. c. or half c. c. used of the normal solution of soda expresses directly the percentage of hydrated or anhydrous acid contained in the examined fluid. For this purpose, the $\frac{1}{10}$ or $\frac{1}{20}$ equivalent number ($H=1$) of grammes of the anhydrous or hydrated acid, are weighed off according as the number of c. c. or half c. c. of normal alkali used, are to express the percentage of hydrated or anhydrous acid contained in the analyzed fluids.

The following are the quantities for the more common acids :—

	$\frac{1}{10}$ Eq. number of grammes.	$\frac{1}{20}$ Eq. number of grammes.
Sulphuric acid	4·0	2·00
Hydrated sulphuric acid	4·9	2·45
Nitric acid	5·4	2·70
Hydrated nitric acid	6·3	3·15
Hydrochloric acid	3·646	1·823
Oxalic acid	3·6	1·80
Crystallized oxalic acid	6·3	3·15
Acetic acid	5·1	2·55
Hydrated acetic acid	6·0	3·00
Tartaric acid	6·6	3·30
Hydrated tartaric acid	7·5	3·75

But, as the weighing of definite small quantities would hardly be accurate enough, it is preferable to weigh off the half eq. grm. of the acids (*i. e.* 20 or 24·5 grm. of sulphuric acid, according to whether it is intended to find the percentage of anhydrous or of hydrated acid; 18·23 of hydrochloric acid, &c.) in a measuring flask holding 500 c. c., add water cautiously,[*] allow to cool if necessary, fill up with water to the mark, shake, and then remove, by means of the pipette, 100 or 50 c. c., according to whether $\frac{1}{10}$ or $\frac{1}{20}$ eq. grm. acid is to be used.

c. Deviations from the preceding method of Analysis.

α. It is often preferred to have the alkali of such a strength that the c. c. or the half c. c. employed to neutralize a round number of grm. or c. c. of an aqueous acid may express at once the percentage of real acid. For instance, if we add 20 c. c. water to 1000 c. c. normal soda solution, these 1020 c. c. will saturate 51 (1 eq.) grm. anhydrous acetic acid, 1000 c. c. therefore saturate 50 grm. Hence if we take 10 grm. of vinegar (10 c. c. will do instead, as the specific gravity of vinegar scarcely differs from that of water), and add our diluted solution of soda to saturation, the c. c. used, divided by 2, will express the percentage of anhydrous acetic acid in the specimen of vinegar examined.*

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[*] In the case of concentrated sulphuric acid, the flask must be half full of water before the acid is weighed into it.

β. If the color of a fluid conceals the change of the dissolved cochineal, or if salts of iron be present, we use red litmus or turmeric paper to hit the point of neutralization, *i. e.*, we add alkali till a strip of test paper dipped in just indicates a weak alkaline reaction. In this case more alkali will be employed than when cochineal can be used in solution, and in exact determinations it may be worth while to rectify the error by a correction. This may be done by taking a like quantity of water and adding soda solution, till the fluid just gives a reaction on the test paper in question, as strong as was obtained at the close of the first experiment. The quantity of alkali used is of course to be deducted from the quantity employed in the first experiment.

d. Application of the Acidimetric principle to the determination of combined acids.

The acidimetric principle may often be employed also for the determination of acids in combination with bases, if solution of carbonate of soda precipitates the latter completely, and in a state of purity. For instance, acetic acid in iron mordant, or in verdigris, may be estimated in this way, by the following process:—Precipitate with a measured quantity of normal solution of carbonate of soda in excess, boil, filter, wash, concentrate the filtrate, add cochineal and normal acid to neutralization. Subtract the c. c. of standard acid used, from the c. c. of soda solution consumed in the experiment: the difference expresses the quantity of soda solution neutralized by the acid contained in the substance, in combination as well as in the free state. Of course, correct results can be expected only if no basic salt has been thrown down by the soda solution.

e. Determination of combined acids by Gibbs' method. See § 149, ii., c, γ, p. 330.

MODIFICATION OF THE COMMON ACIDIMETRIC METHOD (KIEFER†).

§ 205.

Instead of estimating free acid by a solution of soda of known strength, and determining the neutralization point by means of cochineal tincture, an ammoniacal solution of oxide of copper may be used for the purpose, in which case the neutralization point is known by the turbidity observed as soon as the free acid present is completely neutralized. The copper solution is prepared by adding to an aqueous solution of sulphate of copper, solution of ammonia until the precipitate of basic salt which forms at first is just redissolved. After determining the strength of the solution by normal sulphuric or hydrochloric acid (not oxalic), it may be employed for the estimation of all the stronger acids (with the exception of oxalic acid), provided the fluids are clear. The basic salt of copper, in the precipitation of which the final reaction consists, is not insoluble in the ammonia salt formed, and its solubility depends on the degree of concentration, and on the presence of other salts, especially of ammonia salts (CAREY LEA‡). Hence the method cannot boast of scientific

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* Zeitschrift f. analyt. Chem. 1, 253.

† Annal d. Chem. u. Pharm. 93, 386.

‡ Chem. News, 4, 195.

TABLE I.

Percentages of Anhydrous Potassa corresponding to different specific gravities of solution of potassa.

Dalton.		*Tünnermann (at 15°).*			
Specific gravity.	Percentage of anhydrous potassa.	Specific gravity.	Percentage of anhydrous potassa.	Specific gravity.	Percentage of anhydrous potassa.
1·60	46·7	1·3300	28·290	1·1437	14·145
1·52	42·9	1·3131	27·158	1·1308	13·013
1·47	39·6	1·2966	26·027	1·1182	11·882
1·44	36·8	1·2803	24·895	1·1059	10·750
1·42	34·4	1·2648	23·764	1·0938	9·619
1·39	32·4	1·2493	22·632	1·0819	8·487
1·36	29·4	1·2342	21·500	1·0703	7·355
1·33	26·3	1·2268	20·935	1·0589	6·224
1·28	23·4	1·2122	19·803	1·0478	5·002
1·23	19·5	1·1979	18·671	1·0369	3·961
1·19	16·2	1·1839	17·540	1·0260	2·829
1·15	13·0	1·1702	16·408	1·0153	1·697
1·11	9·5	1·1568	15·277	1·0050	0·5658
1·06	4·7				

TABLE II.

Percentages of Anhydrous Soda corresponding to different specific gravities of solution of soda.

Dalton.		*Tünnermann (at 15°).*					
Specific gravity.	Percentage of anhydrous soda.	Specific gravity	Percentage of anhydrous soda.	Specific gravity.	Percentage of anhydrous soda.	Specific gravity.	Percentage of anhydrous soda.
1·56	41·2	1·4285	30·220	1·2982	20·550	1·1528	10·275
1·50	36·8	1·4193	29·616	1·2912	19·945	1·1428	9·670
1·47	34·0	1·4101	29·011	1·2843	19·341	1·1330	9·066
1·44	31·0	1·4011	28·407	1·2775	18·730	1·1233	8·462
1·40	29·0	1·3923	27·802	1·2708	18·132	1·1137	7·857
1·36	26·0	1·3836	27·200	1·2642	17·528	1·1042	7·253
1·32	23·0	1·3751	26·594	1·2578	16·923	1·0948	6·648
1·29	19·0	1·3668	25·989	1·2515	16·319	1·0855	6·044
1·23	16·0	1·3586	25·385	1·2453	15·714	1·0764	5·440
1·18	13·0	1·3505	24·780	1·2392	15·110	1·0675	4·835
1·12	9·0	1·3426	24·176	1·2280	14·506	1·0587	4·231
1·06	4·7	1·3349	23·572	1·2178	13·901	1·0500	3·626
		1·3273	22·967	1·2058	13·297	1·0414	3·022
		1·3198	22·363	1·1948	12·692	1·0330	2·418
		1·3143	21·894	1·1841	12·088	1·0246	1·813
		1·3125	21·758	1·1734	11·484	1·0163	1·209
		1·3053	21·154	1·1630	10·879	1·0081	0·604

TABLE III.

Percentages of AMMONIA (NH_3) corresponding to different specific gravities of solution of ammonia at 16° (J. OTTO).

Specific gravity.	Percentage of ammonia.	Specific gravity.	Percentage of ammonia.	Specific gravity.	Percentage of ammonia.
0·9517	12·000	0·9607	9·625	0·9697	7·250
0·9521	11·875	0·9612	9·500	0·9702	7·125
0·9526	11·750	0.9616	9·375	0·9707	7·000
0·9531	11·625	0·9621	9·250	0·9711	6·875
0·9536	11·500	0·9626	9·125	0·9716	6·750
0·9540	11·375	0·9631	9·000	0·9721	6·625
0·9545	11·250	0·9636	8·875	0·9726	6·500
0·9550	11·125	0·9641	8·750	0·9730	6·375
0·9555	11·000	0·9645	8·625	0·9735	6·250
0·9556	10·950	0·9650	8·500	0·9740	6·125
0·9559	10·875	0·9654	8·375	0·9745	6·000
0·9564	10·750	0·9659	8·250	0·9749	5·875
0·9569	10·625	0·9664	8·125	0·9754	5·750
0·9574	10·500	0·9669	8·000	0·9759	5·625
0·9578	10·375	0·9673	7·875	0·9764	5·500
0·9583	10·250	0·9678	7·750	0·9768	5·375
0·9588	10·125	0·9683	7·625	0·9773	5·250
0·9593	10·000	0·9688	7·500	0·9778	5·125
0·9597	9·875	0·9692	7·375	0·9783	5·000
0·9602	9·750				

accuracy, but as the variations occasioned by the causes mentioned are inconsiderable,* the process retains its applicability to technical purposes, for which, indeed, it was originally proposed. This method is of especial value in cases in which free acid is to be determined in presence of a neutral metallic salt with acid reaction—*e.g.*, free sulphuric acid in mother-liquors of sulphate of copper or sulphate of zinc, &c. It is advisable to determine the strength of the ammoniacal copper solution anew before every fresh series of experiments.

3. ALKALIMETRY.

A. ESTIMATION OF POTASSA, SODA, OR AMMONIA, FROM THE SPECIFIC GRAVITY OF THEIR SOLUTIONS.

§ 206.

In pure or nearly pure solutions of hydrated soda or potassa, or of ammonia, the percentage of alkali may be estimated from the specific gravity of the solution.

B. ESTIMATION OF THE TOTAL AMOUNT OF CARBONATED AND CAUSTIC ALKALI IN CRUDE SODA AND IN POTASHES.

The "soda ash" of commerce is a crude carbonate of soda—the

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* Compare my experiments on the subject in the Zeitschrift f. analyt. Chem. 1, 108.

"potashes" and "pearlash" a crude carbonate of potash. The commercial value of these articles depends on the percentage of alkaline carbonate (or caustic alkali) that they contain, which is very variable.

I. Volumetric Methods.

Method of Descroizilles *and* Gay-Lussac, *slightly modified.*

§ 207.

The principle of this method is the converse of that on which the acidimetric method described § 204, is based, *i.e.*, if we know the quantity of an acid of known strength, required to saturate an unknown quantity of caustic potassa or soda, or of carbonate of potassa or soda, we may readily calculate from this the amount of alkali present.

For technical analyses we may employ the normal sulphuric acid, p. 493.

For the analysis we may conveniently weigh off such a quantity of the substance that the number of c. c. of acid required to neutralize it shall directly express its percentage of the alkali or carbonate sought.

The proper quantities of the compounds of potassa and soda to employ are $\frac{1}{16}$ Eq. ($H = 1$) expressed in grms., viz.:—

Potassa, $K\ O$	4·711	grm.
Hydrate of potassa, KO, HO	5·611	"
Carbonate of potassa, KO, CO_2	6·911	"
Bicarbonate of potassa, $KO, HO, 2\ CO_2$	10·011	"
Soda, NaO	3·100	"
Hydrate of soda, $NaO\ HO$	4·000	"
Carbonate of soda (dry) $NaO\ CO_2$	5·300	"
Crystallized carbonate of soda, $NaO\ CO_2, 10\ HO$	14·300	"
Bicarbonate of soda, $NaO\ HO\ 2\ CO_2$	8·400	"

With regard to the examination of pearlash by this method, the following points deserve attention:—

The various sorts of potash of commerce contain, besides carbonate of (and caustic) potassa,

a. Neutral salts (*e.g.*, sulphate of potassa, chloride of potassium).

b. Salts with alkaline reaction (*e.g.*, silicate of potassa, phosphate of potassa).

c. Admixtures insoluble in water, more especially carbonate, phosphate, and silicate of lime.

The salts named in *a* exercise no influence upon the results, but not so those named in *b* and *c*. Those in *c* may be removed by filtration; but the admixture of the salts named in *b* constitutes an irremediable, though slight source of error:—that is to say, if it is desired to confine the determination to the caustic and carbonated alkali. But as regards the estimation of the value of pearlash for many purposes, the term error cannot be applied; as, for instance, in the preparation of caustic potassa, by boiling the solution with lime, the alkali combined with silicic acid and with phosphoric acid is converted, like the carbonate, into the caustic state.

If you are not satisfied with finding the percentage of available alkali, but desire also to know whether the remainder consists simply of foreign salts, or whether water is also present, the determination of the latter substance must precede the alkalimetric examination. The same remark applies also to soda.

With regard to the examination of soda by this method, the following points deserve attention:—

The soda of commerce, prepared by LEBLANC's method, contains, besides carbonate of soda, always, or at least generally, hydrate of soda, sulphate of soda, chloride of sodium, silicate and aluminate of soda, and not seldom also sulphide of sodium, hyposulphite and sulphite of soda.*

The three last-named substances impede the process, and interfere more or less with the accuracy of the results. Their presence is ascertained in the following way:—

a. Mix with sulphuric acid; a smell of sulphuretted hydrogen reveals the presence of *sulphide of sodium*, with which hyposulphite of soda is also invariably associated.

b. Color dilute sulphuric acid with a drop of solution of permanganate of potassa or chromate of potassa, and add some of the soda under examination, but not sufficient to neutralize the acid. If the solution retains its color, this proves the absence of both sulphite and hyposulphite of soda; but if the fluid loses its color, or turns green, as the case may be, one of these salts is present.

c. Whether the reaction described in *b* proceeds from sulphite or hyposulphite of soda, is ascertained by supersaturating a clear solution of the sample under examination with hydrochloric acid. If the solution, after the lapse of some time, becomes turbid, owing to the separation of sulphur (emitting at the same time the odor of sulphurous acid), this may be regarded as a proof of the presence of hyposulphite of soda; however, the solution may, besides the hyposulphite, also contain sulphite of soda. With respect to the detection of sulphite of soda in the presence of hyposulphite, comp. "Qual. Anal.," p. 187.

The defects arising from the presence of the three compounds in question may be remedied in a measure, by igniting the weighed sanple of the soda with chlorate of potassa, before proceeding to saturate it. This operation converts the sulphide of sodium, hyposulphite of soda, and sulphite of soda into sulphate of soda. But if hyposulphite of soda is present, the process serves to introduce another source of error, as that salt, upon its conversion into sulphate of soda, decomposes an equivalent of carbonate of soda, and expels the carbonic acid of the latter [$Na\,O, S_2O_2 + 4\,O$ (from the chlorate of potassa) $+ Na\,O, CO_2 = 2\,(Na\,O, SO_3) + CO_2$].

The presence of silicate of soda and of aluminate of soda may be generally recognized by the separation of a precipitate as soon as the solution is saturated with acid. If you intend the result to express the quantity of carbonated and caustic alkali only, the presence of these two bodies becomes a slight source of error, but if you wish to estimate the value of the soda for many purposes, no error will be caused.

§ 208.

Method of FR. MOHR, *modified.*

Instead of estimating the alkalies in the direct way by means of an acid of known strength, we may estimate them also, as proposed first by FR. MOHR,* by supersaturating with standard acid, expelling the carbonic acid by boiling, and finally by determining by solution of soda the excess of standard acid added.

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* Traces of cyanide of sodium are also occasionally found.

This process gives very good results, and is therefore particularly suited for scientific investigations. It requires the standard fluids mentioned in § 204, viz., a standard acid and standard solution of soda. Each of these fluids is filled into a MOHR's burette.

The process is as follows:—

Dissolve the alkali in water, and add a measured quantity of tincture of cochineal; run in now as much of the normal acid as will suffice to impart an orange tint to the fluid; then boil, and remove the last traces of carbonic acid, by boiling, shaking, blowing into the flask, and finally sucking out the air.

Now add standard solution of soda, drop by drop, until the color just appears violet. There is no difficulty in determining the exact point at which the reaction is completed.

If the standard solution of soda and the normal acid are of corresponding strength, the number of c. c. used of the soda solution is simply deducted from the number of c. c. used of the acid. The remainder expresses the quantity of acid neutralized by the alkali in the examined sample. If the two standard fluids are not of corresponding strength, the excess of acid added, and subsequently neutralized by the soda solution, is calculated from the known proportion the one bears to the other.

If $\frac{1}{10}$ eq. number ($H=1$) of grammes have been weighed of the alkalies to be valued, of soda accordingly, 5·3 grm., of pearlash 6·91 grm., the number of c. c. used of the normal acid expresses directly the percentage of carbonate of soda or carbonate of potassa contained in the examined sample; since 100 c. c. of the normal acid, containing $\frac{1}{10}$ eq. grm. acid will just suffice to neutralize $\frac{1}{10}$ eq. grm. pure carbonate of soda or carbonate of potassa.† If any other quantities of the alkalies have been weighed off, a simple calculation will give the result in the desired form.

To make this simple calculation quite clear for all possible cases, I select one of the most complicated kind, proceeding upon the supposition that the soda solution is not of corresponding strength with the normal acid, but that 2·2 c. c. of the soda solution neutralize 1 c. c. of the acid; and that instead of $\frac{1}{10}$ eq. grm., 3·71 grm. of pearlash have been weighed off.

The quantity of acid added was 48 c. c.; the excess required 4·3 c. c. of soda solution for neutralization. The proportion

$$2{\cdot}2 : 1 :: 4{\cdot}3 : x;\ x=1{\cdot}95$$

shows that the excess of acid was 1·95 c. c.; 48 – 1·95   46·05 c. c. of the acid have accordingly been consumed by the pearlash. The proportion

$$3{\cdot}71 : 46{\cdot}05 :: 6{\cdot}91\ (\tfrac{1}{10}\text{ eq. KO, CO}_2) : x;\ x=85{\cdot}77$$

shows that the examined pearlash contains 85·77 per cent. of the pure carbonate.

With regard to certain variations from the ordinary course which are occasionally convenient, comp. p. 495.

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* Annal. d. Chem. u. Pharm. 86, 129.

† Of 100 per cent.

§ 209.

There now still remain two questions to be considered, which are of importance for the estimation of the commercial value of potash and soda. The first concerns the separate determination of the caustic alkali, which the sample under examination may contain besides the carbonate; the second, the determination of carbonate of soda in presence of carbonate of potassa.

C. DETERMINATION OF THE CAUSTIC ALKALI WHICH COMMERCIAL ALKALI MAY CONTAIN BESIDE THE CARBONATE.

Many kinds of potashes and crude soda, more especially the latter, contain, besides alkaline carbonate, also caustic alkali; and the chemist is often called upon to determine the amount of the latter; as it is, for instance, by no means a matter of indifference to the soap-boiler how much of the soda is supplied to him already in the caustic state. This may be effected as follows:

Weigh off $\frac{3}{10}$ eq. grm. substance; of potashes accordingly, 20·73 grm., of soda 15·9 grm.; dissolve in water, in a flask holding 300 c. c., fill up to the mark, shake, allow the fluid to deposit out of contact of air, and take out two portions of 100 c. c. each. Determine in the one portion the total quantity of the carbonated and caustic alkali, as directed § 208; the number of c. c. of normal acid used expresses the amount of caustic alkali + alkaline carbonate, in per-cents. of the latter. Transfer the other portion to a measuring-flask holding 300 c. c., add 100 c. c. of water, then solution of chloride of barium as long as a precipitate forms, add water up to the mark, shake, allow to deposit out of contact of air,* measure off 100 c. c. of the supernatant clear fluid—which now contains caustic baryta in corresponding quantity to the caustic alkali present in the sample—add some tincture of cochineal, then normal *nitric acid* (see § 210), to acid reaction. Neutralize the excess of acid by normal solution of soda, and you will find the c. c. of normal acid that have been required by the caustic baryta. Multiply this by 3 (as only $\frac{1}{3}$ of the second portion has been employed in the experiment); the result gives the percentage of caustic alkali, expressed as carbonate of soda or potassa. Deduct this number from the percentage obtained in the first experiment; the difference gives the quantity of carbonate of potassa or soda present as such. To calculate the caustic alkali into the anhydrous or hydrated state, it is only necessary to multiply by the numbers given in the first method.

D. ESTIMATION OF CARBONATE OF SODA IN PRESENCE OF CARBONATE OF POTASSA.

Soda being much cheaper than potash, is occasionally used to adulterate the latter. The common alkalimetric methods not only fail to detect this adulteration, but they give the admixed soda as carbonate of potassa. Many processes† have been proposed for estimating in a simple way the soda contained in potash, but not one of them can be said to satisfy the requirements of the case.

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* Filtering through a dry filter causes the caustic alkali to come out rather too low, as the paper retains caustic baryta (A. Müller, Journ. f. prakt. Chem. 83, 384; Zeitschrift f. analyt. Chem. 1, 84).

† Comp. Handwörterbuch der Chemie, 2 Aufl. I. 443.

The following tolerably expeditious process, however, gives accurate results:—Dissolve 6·25 grm. of the gently ignited pearlash in water, filter the solution into a quarter-litre flask, add acetic acid in slight excess, apply a gentle heat until the carbonic acid is expelled, then add to the fluid, while still hot, acetate of lead, drop by drop, until the formation of a precipitate of sulphate of lead *just* ceases; allow the mixture to cool, add water up to the mark, shake, allow to deposit, filter through a dry filter, and transfer 200 c. c. of the filtrate, corresponding to 5 grm. of pearlash, to a ¼-litre flask. Add sulphuretted hydrogen water up to the mark, and shake. If the acetate of lead has been carefully added, the fluid will now smell of sulphuretted hydrogen, and no longer contain lead; in the contrary case, sulphuretted hydrogen gas must be conducted into it. After the sulphide of lead has subsided, filter through a dry filter. Evaporate 50 c. c. of the filtrate (corresponding to 1 grm. of pearlash) with addition of 10 c. c. hydrochloric acid, of 1·10 sp. gr., in a weighed platinum dish, to dryness, then cover the dish, heat, and weigh; the weight found expresses the total quantity of chloride of potassium and chloride of sodium given by 1 grm. of the pearlash. Estimate the potassa and soda now severally in the indirect way, by determining the chlorine volumetrically (§ 141, I., *b*). For the calculation of the results, see § 197.

4. Estimation of Alkaline Earths by the Alkalimetric Method.

§ 210.

Alkaline earths, in the caustic state or in the form of carbonates, may also be estimated by means of a standard acid. Standard sulphuric acid may be used for the estimation of magnesia; standard nitric acid for that of baryta, strontia, and lime. To prepare 1 litre of normal nitric acid you require a pure dilute nitric acid of about 1·04 sp. gr., and also a normal soda solution (or at least a soda solution whose relation to normal sulphuric acid is exactly known).

Fill a Mohr's burette with the nitric acid, measure off 20 c. c.; color with tincture of cochineal and add normal solution of soda from a second burette to alkaline reaction. Repeat the experiment. Suppose 20 c. c. of the acid have required 24 c. c. of normal soda solution, add to every 20 volumes of the acid 4 volumes of water. For the proper way of effecting the dilution, see p. 493 (Preparation of Normal Sulphuric Acid). After diluting, measure off 20 c. c., and neutralize with the normal solution of soda, of which it must now take exactly 20 c. c.

It will be well to verify the normal nitric acid in the manner directed, p. 492.

If the alkaline earth to be estimated is in the caustic state, weigh off a definite quantity, add water, then, from a burette normal nitric acid, until solution is effected, and the fluid, colored with cochineal, appears orange; now add soda solution until the color just changes to violet; deduct the soda solution added from the acid, and calculate by the proportion

1000 (c. c.) : the number of c. c. of acid used

::

76·5 (eq. baryta), 51·75 (eq. strontia), 28 (eq. lime) or 20 (eq. magnesia) : x (grm. of baryta, strontia, lime, or magnesia).

Should there be a failure the first time in determining the exact point at which the fluids turn violet, add another c. c. of the acid, and then again solution of soda until violet.

In the case of carbonates of the alkaline earths, heat a weighed quantity of the sample, in a flask, with water; then add, from the burette small portions of normal nitric acid. When solution is effected and the acid is consequently in excess, add tincture of cochineal, then normal soda solution, till only a small excess of acid remains, say $\frac{1}{2}$ or 1 c. c. Heat to boiling, shake the liquid, and continue boiling for some minutes, to expel the carbonic acid completely from the fluid and flask; finally add soda until just violet. 1000 c. c. of the normal acid correspond to 98·5 grm. carbonate of baryta, 73·75 grm. carbonate of strontia, 50 grm. carbonate of lime, or 42 grm. carbonate of magnesia.

By weighing off the $\frac{1}{10}$ or $\frac{1}{20}$ eq. $(H=1)$ grm. of the caustic or carbonated alkaline earths, the necessity of a calculation of the results is altogether dispensed with; in the former case, the number of c. c., in the latter that of half c. c. used of the normal acid, expresses the percentage required.

5. CHLORIMETRY.

§ 211.

The "chloride of lime," or "bleaching powder" of commerce, contains hypochlorite of lime, chloride of calcium, and hydrate of lime. The two latter ingredients are for the most part combined with one another to basic chloride of calcium. In freshly prepared and perfectly normal chloride of lime, the quantities of hypochlorite of lime and chloride of calcium present stand to each other in the proportion of their equivalents. When such chloride of lime is brought into contact with dilute sulphuric acid, the whole of the chlorine it contains is liberated in the elementary form, in accordance with the following equation:—

$$Ca\,O,\,Cl\,O + Ca\,Cl + 2\,(H\,O,\,S\,O_3) = 2\,(Ca\,O,\,S\,O_3) + 2\,H\,O + 2\,Cl.$$

On keeping chloride of lime, however, the proportion between hypochlorite of lime and chloride of calcium gradually changes—the former decreases, the latter increases. Hence from this cause alone, to say nothing of original difference, the commercial article is not of uniform quality, and on treatment with acid gives sometimes more and sometimes less chlorine.

As the value of this article depends entirely upon the amount of chlorine set free on treatment with acid, chemists have devised various simple methods of determining the available amount of chlorine in any given sample. These methods haye collectively received the name of Chlorimetry. We describe a few of the best.

PREPARATION OF THE SOLUTION OF CHLORIDE OF LIME.

The solution is prepared alike for all methods, and best in the following manner:—

Weigh off 10 grm., triturate finely with a little water, add gradually more water, pour the liquid into a litre flask, triturate the residue again with water, and rinse the contents of the mortar carefully into the flask; fill the latter to the mark, shake the milky fluid, and examine it at once in that state, *i.e.*, without allowing it to deposit; and every time, before measuring off a fresh portion, shake again. The results obtained with this turbid solution are much more constant and correct than when, as is usually recommended, the fluid is allowed to deposit, and the experiment is made with the supernatant clear portion alone. The truth of this may readily be proved by making two separate experiments, one with the decanted clear fluid, and the other with the residuary turbid mixture. Thus, for instance, in an experiment made in my own laboratory, the decanted clear fluid gave 22·6 of chlorine, the residuary mixture 25·0, the uniformly mixed turbid solution 24·5.

1 c. c. of the solution of chloride of lime so prepared corresponds to 0.01 grm. chloride of lime.

A. PENOT'S *Method.*[*]

§ 212.

This method is based upon the conversion of arsenious acid into arsenic acid; the conversion is effected in an alkaline solution. Iodide of potassium-starch paper is employed to ascertain the exact point when the reaction is completed.

a. Preparation of the Iodide of Potassium-Starch Paper.

The following method is preferable to the original one given by PENOT:—

Stir 3 grm. of potato starch in 250 c. c. of cold water, boil with stirring, add a solution of 1 grm. iodide of potassium and 1 grm. crystallized carbonate of soda, and dilute to 500 c. c. Moisten strips of fine white unsized paper with this fluid, and dry. Keep in a closed bottle.

b. Preparation of the Solution of Arsenious Acid.

Dissolve 4·436 grm. of pure arsenious acid and 13 grm. pure crystallized carbonate of soda in 600—700 c. c. water, with the aid of heat, let the solution cool, and then dilute to 1 litre. Each c. c. of this solution contains 0·004436 grm. arsenious acid which corresponds to 1 c. c. chlorine gas of 0° and 760 mm. atmospheric pressure.[†]

As arsenite of soda in alkaline solution is liable, when exposed to access of air, to be gradually converted into arseniate of soda, PENOT'S solution should be kept in small bottles with glass stoppers, filled to the top, and a fresh bottle used for every new series of experiments.

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[*] Bulletin de la Société Industrielle de Mulhouse, 1852, No. 118.—Dingler's Polytech. Journal, 127, 134.

[†] Penot gives the quantity of arsenious acid as 4·44; but I have corrected this number to 4·436, in accordance with the now received equivalents of the substances and specific gravity of chlorine gas—after the following proportion:—
70·92 (2 eq. chlorine) : 99 (1 eq. AsO_3) :: 3·17763 (weight of 1 litre of chlorine gas) : x; $x=4·436$, *i.e.* the quantity of arsenious acid which 1 litre of chlorine gas converts into arsenic acid.

This solution is arranged to suit the foreign method of designating the strength of chloride of lime—viz., in chlorimetrical degrees (each degree represents 1 litre chlorine gas at 0° and 760 mm. pressure in a kilogramme of the substance). This

According to Fr. Mohr * the solution keeps unchanged, if the arsenious acid and the carbonate of soda are both *absolutely* free from oxidizable matters (sulphide of arsenic, sulphide of sodium, sulphite of soda).

c. *The Process.*

Measure off, with a pipette, 50 c. c. of the solution of chloride of lime prepared according to the directions of § 211, transfer to a beaker, and from a 50 c. c. burette, add, slowly, and at last drop by drop, the solution of arsenious acid, with constant stirring, until a drop of the mixture produces no longer a blue-colored spot on the iodized paper; it is very easy to hit the point exactly, as the gradually increasing faintness of the blue spots made on the paper by the fluid dropped on it, indicates the approaching termination of the reaction, and warns the operator to confine the further addition of the solution of arsenious acid to a single drop at a time. The number of ½ c. c. used indicates directly the number of chlorimetrical degrees (see note), as the following calculation shows: suppose you have used 40 c. c. of solution of arsenious acid, then the quantity of chloride of lime used in the experiment contains 40 c. c. of chlorine gas. Now, the 50 c. c. of solution employed correspond to 0·5 grm. of chloride of lime; therefore 0·5 grm. of chloride of lime contain 40 c. c. chlorine gas, therefore 1000 grm. contain 80000 c. c. ≐ 80 litres. This method gives very constant and accurate results, and appears to be particularly well suited for use in manufacturing establishments where there is no objection, on the score of danger, to the employment of arsenious acid. (Expt. No. 99.)

B. Otto's *Method.*

§ 213.

The principle of this method is as follows:—

Two eq. protosulphate of iron, when brought into contact with chlorine, in presence of water and free sulphuric acid, give 1 eq. sesquisulphate of iron, and 1 eq. H Cl, the process consuming 1 eq. chlorine.

$$2\,(\mathrm{Fe\,O,\,S\,O_3}) + \mathrm{S\,O_3} + \mathrm{H\,O} + \mathrm{Cl} = \mathrm{Fe_2\,O_3,\,3\,S\,O_3} + \mathrm{H\,Cl}$$

2 eq. crystallized protosulphate of iron:—

$$2\,(\mathrm{Fe\,O,\,S\,O_3,\,H\,O} + 6\,\mathrm{aq.}) = 278$$

correspond to 35·46 of chlorine, or, in other terms, 0·7839 grm. crystallized protosulphate of iron correspond to 0·1 grm. chlorine.

The protosulphate of iron required for these experiments is best prepared as follows:—

Take iron nails, free from rust, and dissolve in dilute sulphuric acid, applying heat in the last stage of the operation; filter the solution,

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method was proposed by Gay-Lussac. The degrees may readily be converted into per-cents, and *vice versâ*, thus:—A sample of chloride of lime of 90° contains 90 × 3·17763 = 285·986 grm. chlorine in 1000 grm. or 28·59 in 100; and a sample containing 34·2 per cent. chlorine, is of 107·6°, for 100 grm. of the substance contain 34·2 grm. chlorine ∴ 1000 grm. of the substance contain 342 grm. chlorine, but 342 grm. chlorine = $\frac{342}{3\cdot17763}$ litres = 107·6 litres ∴ 1000 grm. of the substance contain 107·6 litres chlorine.

* His Lehrbuch der Titrirmethode, 2 Aufl. S. 290.

still hot, into about twice its volume of spirit of wine. The precipitate consists of

$$Fe\,O,\,S\,O_3+H\,O+6\text{ aq.}$$

Collect upon a filter, wash with spirit of wine, spread upon a sheet of blotting paper, and dry in the air. When the mass smells no longer of spirit of wine, transfer to a bottle and keep this well corked. Instead of protosulphate of iron, sulphate of protoxide of iron and ammonia (p. 93) may be used. 0·1 grm. of chlorine oxidizes 1·1055 grm. of this double sulphate.

The Process.

Dissolve 3·1356 grm. (4 × ·07839 grm.) of the precipitated protosulphate of iron, or 4·422 grm. (4 × 1·1055 grm.) of sulphate of protoxide of iron and ammonia, with addition of a few drops of dilute sulphuric acid, in water, to 200 c. c.; take out, with a pipette, 50 c. c., corresponding to 0·7839 grm. protosulphate of iron, or 1·1055 grm. sulphate of protoxide of iron and ammonia, dilute with 150—200 c. c. water, add a sufficiency of pure hydrochloric acid, and run in from a 50 c. c. burette the freshly shaken solution of chloride of lime, prepared according to § 211, until the protoxide of iron is completely converted into sesquioxide. To know the exact point when the oxidation is completed, place a number of drops of a solution of ferricyanide of potassium on a plate, and, when the operation is drawing to an end, apply some of the mixture with a stirring-rod to one of the drops on the plate, and observe whether it produces a blue precipitate; repeat the experiment after every fresh addition of two drops of the solution of choride of lime. When the mixture no longer produces a blue precipitate in the solution of ferricyanide of potassium on the plate, read off the number of volumes used of the solution of chloride of lime.

The amount of solution of chloride of lime used contained 0·1 grm. of chlorine. Suppose 40 c. c. have been used: as every c. c. corresponds to 0·01 grm. of chloride of lime, the percentage by weight of available chlorine in the chloride of lime is found by the following proportion:—

$$0{\cdot}40 : 0{\cdot}10 :: 100 : x;\ x=25;$$

or, by dividing 1000 by the number of c. c. used of the solution of chloride of lime.

This method also gives very satisfactory results, provided always that the salts of protoxide of iron are perfectly dry and free from sesquioxide.

Modification of the preceding Method.

Instead of the solution of protosulphate of iron, a solution of protochloride of iron, prepared by dissolving pianoforte wire in hydrochloric acid (according to p. 194, *aa*), may be used with the best results. If 0·6316 of pure metallic iron, *i.e.*, 0·6335 of fine pianoforte wire (which may be assumed to contain 99·7 per cent. of iron), are dissolved to 200 c. c., the solution so prepared contains exactly the same amount of iron as the solution of protosulphate above mentioned—that is to say, 50 c. c. of it correspond to 0·1 grm. chlorine. But as it is inconvenient to weigh off a definite quantity of iron wire, the following course may be pursued in preference: weigh off, accurately, about 0·15 grm., dissolve, dilute the solution to about 200 c. c., oxidize the iron with the solution of chloride of lime, prepared according to the directions of § 211, and calculate the chlorine by the proportion

$$56 : 35{\cdot}46 :: \text{the quantity of iron used} : x ;$$

the *x* found corresponds to the chlorine contained in the amount used of the solution of chloride of lime. This calculation may be dispensed with by the application of the following formula, in which the carbon in the pianoforte wire is taken into account:—

Multiply the weight of the pianoforte wire by 6313, and divide the product by the number of c. c. used of the solution of chloride of lime: the result expresses the percentage of chlorine by weight.

This method gives very good results. I have described it here principally because it dispenses altogether with the use of standard fluids. It is therefore particularly well adapted for occasional examinations of samples of chloride of lime, and also by way of control. (See Expt. No. 99.)

C. Bunsen's *Method.*

Pour 10 c. c. of the solution of chloride of lime, prepared according to the directions of § 211 (containing 0·1 chloride of lime), into a beaker, and add about 6 c. c. of the solution of iodide of potassium, prepared according to p. 314, *a* (containing 0·6 KI); dilute the mixture with about 100 c. c. water, acidify with hydrochloric acid, and determine the liberated iodine as directed § 146. As 1 eq. iodine corresponds to 1 eq. chlorine, the calculation is easy. This method gives excellent results. (Compare Expt. No. 99.)

6. Examination of Black Oxide of Manganese.

§ 214.

The native black oxide of manganese (as also the regenerated artificial product) is a mixture of binoxide of manganese with lower oxides of that metal, and with sesquioxide of iron, clay, &c.; it also invariably contains moisture, and frequently chemically combined water. The commercial value of the article depends entirely upon the amount of binoxide (or, more correctly expressed, of available oxygen) which it contains. By "available oxygen" we understand the excess of oxygen contained in a manganese, over the 1 eq. combined with the metal to protoxide; upon treating the ore with hydrochloric acid, an amount of chlorine is obtained equivalent to this excess of oxygen. This available oxygen is always expressed in the form of binoxide of manganese. 1 eq. corresponds to 1 eq. binoxide of manganese, since $MnO_2 = MnO + O$.

I. Drying the Sample.

All analyses of manganese proceed of course upon the supposition that the sample operated upon is a fair average specimen of the ore. A portion of a tolerably finely powdered average sample is generally sent for analysis to the chemist; in the case of new lodes, however, a number of samples, taken from different parts of the mine, are also occasionally sent. If, in the latter case, the average composition of the ore is to be ascertained, and not simply that of the several samples, the following course must be resorted to: crush the several samples of the ore in an iron mortar to coarse powder, and pass the whole of this through a rather coarse sieve. Mix uniformly, then remove a sufficiently large portion of the coarse powder with a spoon, reduce it to powder in a steel mortar, passing the whole of this through a fine sieve. Mix the powder obtained by this second process of pulverization most intimately; take about 8—10 grm. of it, and triturate this, in small portions at a time, in an agate mortar, to an impalpable powder. Average samples are generally already sufficiently fine to require only the last operation.

As regards the temperature at which the powder is to be dried, if you desire to expel the whole of the moisture without disturbing any of the water of hydration, the temperature adopted must be 120° (this is the result of my own experiments, see Expt. No. 100). But, as there appears to be at present an almost universal understanding in the manganese trade, to limit the drying temperature to 100°, the fine powder is exposed, in a shallow copper or brass pan, for 6 hours, to the temperature of boiling water, in a water-bath (p. 37, fig. 19).

When the samples have been dried, they are introduced, still hot, into glass tubes 12—14 cm. long, and 8—10 mm. wide, sealed at one end; these tubes are then corked and allowed to cool.

In laboratories where whole series of analyses of different ores are of frequent occurrence, it is advisable to number the drying-pans and glass tubes, and to transfer the samples always from the pan to the tube of the corresponding number.

II. Determination of the Binoxide of Manganese.

§ 215.

Of the many methods that have been proposed for the valuation of manganese ores, I select three as the most expeditious and accurate. The first is more particularly adapted for technical purposes.

A. Fresenius *and* Will's *Method.*

a. If oxalic acid (or an oxalate) is brought into contact with binoxide of manganese, in presence of water and excess of sulphuric acid, protosulphate of manganese is formed, and carbonic acid evolved, while the oxygen, which we may assume to exist in the binoxide of manganese in combination with the protoxide, combines with the elements of the oxalic acid, and thus converts the latter into carbonic acid.

$$\mathrm{Mn\,O_2 + SO_3 + C_2O_3 = Mn\,O, SO_3 + 2\,C\,O_2}.$$

Each equivalent of available oxygen or, what amounts to the same, each 1 eq. binoxide of manganese = 43·5, gives 2 eq. carbonic acid = 44.

b. If this process is performed in a weighed apparatus from which nothing except the evolved carbonic acid can escape, and which, at the same time, permits the complete expulsion of that acid, the diminution of weight will at once show the amount of carbonic acid which has escaped, and consequently, by a very simple calculation, the quantity of binoxide contained in the analyzed manganese ore. As 44 parts by weight of carbonic acid correspond to 43·5 of binoxide of manganese, the carbonic acid found need simply be multiplied by 43·5, and the product divided by 44, or the carbonic acid may be multiplied by

$$\frac{43\cdot5}{44}=0\cdot9887,$$

to find the corresponding amount of binoxide of manganese.

c. But even this calculation may be avoided by simply using in the operation the exact weight of ore which, if the latter consisted of pure binoxide, would give 100 parts of carbonic acid.

The number of parts evolved of carbonic acid expresses, in that case, directly the number of parts of binoxide contained in 100 parts of the analyzed ore. It results from *b* that 98·87 is the number required. Suppose the experiment is made with 0·9887 grm. of the ore, the number of centigrammes of carbonic acid evolved in the process expresses directly the percentage of binoxide contained in the analyzed manganese ore. Now, as the amount of carbonic acid evolved from 0·9887 grm. of manganese would be rather small for accurate weighing, it is advisable to take a multiple of this weight, and to divide afterwards the number of centigrammes of carbonic acid evolved from this multiple weight by the same number by which the unit has been multiplied. The multiple which answers the purpose best for superior ores is the triple, = 2·966; for inferior ores, I recommend the quadruple, = 3·955, or the quintuple, = 4·9435.

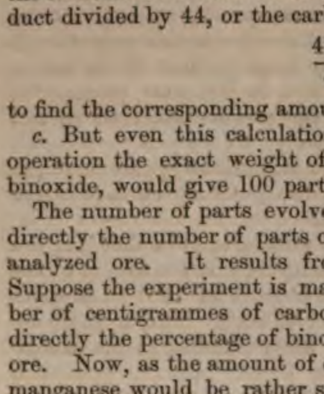

Fig. 100.

The analytical process is performed in the apparatus illustrated in fig. 100, and which has been described already, p. 289.

The flask *A* should hold, up to the neck, about 120 c.c.; *B* about 100 c.c. The latter is half filled with sulphuric acid; the tube *a* is closed at *b* with a little wax ball, or a very small piece of caoutchouc tubing, with a short piece of glass rod inserted in the other end.

Place 2·966, or 3·955, or 4·9435 grm.—according to the quality of the ore—in a watch-glass, and tare the latter most accurately on a delicate balance; then remove the weights from the watch-glass, and replace them by manganese from the tube, very cautiously, with the aid of a gentle tap with the finger, until the equilibrum is exactly restored. Transfer the weighed sample, with the aid of a card, to the flask *A*, add 5—6 grm. neutral oxalate of soda, or about 7·5 grm. neutral oxalate of potassa, in powder, and as much water as will fill the flask to about one-third. Insert the cork into *A*, and tare the apparatus on a strong but delicate balance, by means of shot, and lastly tinfoil, not placed directly on the scale, but in an appropriate vessel. The tare is kept under a glass bell. Try whether the apparatus closes air-tight (see p. 289). Then make some sulphuric acid flow from *B* into *A*, by applying suction to *d*, by means of a caoutchouc tube. The evolution of carbonic acid commences immediately in a steady and uniform manner. When it begins to slacken, cause a fresh portion of sulphuric acid to pass into *A*, and repeat this until the manganese ore is completely decomposed, which, if the sample has been very finely pulverized, requires at the most about five minutes. The complete decomposition of the analyzed ore is indicated, on the one hand, by the cessation of the disengagement of carbonic acid, and its non-renewal upon the influx of a fresh portion of sulphuric acid into *A*; and, on the other hand, by the total disappearance of every trace of black powder from the bottom of *A*.*

Now cause some more sulphuric acid to pass from *B* into *A*, to heat the fluid in the latter, and expel the last traces of carbonic acid therein dissolved; remove the wax stopper, or india-rubber tube, from *b*, and apply gentle suction to *d* until the air drawn out tastes no longer of carbonic acid. Let the apparatus cool completely in the air, and place it on the balance, with the tare on the other scale, and restore equilibrium. The number of centigramme weights added, divided by 3, 4, or 5, according to the multiple of 0·9887 grm. used, expresses the percentage of binoxide contained in the analyzed ore.

In experiments made with definite quantities of the ore, weighing in an open watch-glass cannot well be avoided, and the dried manganese is thus exposed to the chance of a reabsorption of water from the air, which of course tends to interfere, to however so trifling an extent, with the accuracy of the results. In very precise experiments, therefore, the best way is to analyze an indeterminate quantity of the ore, and to calculate the percentage as shown above. For this purpose, one of the little corked tubes, filled with the dry pulverized ore, is accurately weighed, and about 3 to 5 grm. (according to the quality of the ore) are transferred to the flask *A*. By now reweighing the tube, the exact quantity of ore in the flask is ascertained. To facilitate this operation, it is advisable to scratch on the tube, with a file, marks indicating, approximately, the various quantities which may be required for the analysis, according to the quality of the ore.

With proper skill and patience on the part of the operator, a good balance and correct weights, this method gives most accurate and corresponding results, differing in two analyses of the same ore barely to the extent of 0·2 per cent.

If the results of two assays differ by more than 0·2 per cent., a third experiment should be made. In laboratories where analyses of manganese ores are matters of frequent occurrence, it will be found convenient to use an aspirator for sucking out the carbonic acid. In the case of very moist air, the error which proceeds from the fact that the water in the air drawn through the apparatus is retained, and which is usually quite inconsiderable, may now be increased to an important extent. Under such circumstances, connect the end of the tube *b* with a chloride of calcium tube during the suction.

Some ores of manganese contain *carbonates of the alkaline earths*, which of course necessitates a modification of the foregoing process. To ascertain whether carbonates of the alkaline earths are present, boil a sample of the pulverized ore with water, and add nitric acid. If any effervescence takes place, the process is modified as follows (RÖHR †):—

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* If the manganese ore has been pulverized in an iron mortar, a few black spots (particles of iron from the mortar) will often remain perceptible.

† Zeitschrift f. analyt. Chem. 1, 48.

After the weighed portion of ore has been introduced into the flask *A*, treat it with water, so that the flask may be about ¼ full, add a few drops of dilute sulphuric acid (1 part, by weight, sulphuric acid, to 5 parts water) and warm with agitation, preferably in a water bath. After some time dip a rod in and test whether the fluid possesses a strongly acid reaction. If it does not, add more sulphuric acid. As soon as the whole of the carbonates are decomposed by continued heating of the acidified fluid, completely neutralize the excess of acid with soda solution free from carbonic acid, allow to cool, add the usual quantity of oxalate of soda, and proceed as above.

If you have no soda solution free from carbonic acid at hand, you may place the oxalate of soda or oxalic acid (about 3 grm.) in a small tube, and suspend this in the flask *A* by means of a thread fastened by the cork. When the apparatus is tared, and you have satisfied yourself that it is air-tight, release the thread and proceed as above.

B. Bunsen's *Method.*

Reduce the ore to the very finest powder, weigh off about 0·4 grm., introduce this into the small flask *a*, illustrated in fig 59, p. 308, and pour pure fuming hydrochloric acid over it; conduct the process exactly as in the analysis of chromates. Boil until the ore is completely dissolved and all the chlorine expelled, which is effected in a few minutes. Each eq. iodine separated corresponds to 1 eq. chlorine evolved, and accordingly to 1 eq. binoxide of manganese. For the estimation of the separated iodine, the method § 146 may be employed. Results most accurate.

C. *Estimation of the Binoxide of Manganese by means of Iron.*

Dissolve, in a small long-necked flask, placed in a slanting position, about 1 grm. pianoforte wire, accurately weighed, in moderately concentrated pure hydrochloric acid; weigh off about 0·6 grm. of the sample of manganese ore in a little tube, drop this into the flask, with its contents, and heat cautiously until the ore is dissolved. 1 eq. binoxide of manganese converts 2 eq. of dissolved iron from the state of proto- to that of sesquichloride. When complete solution has taken place, dilute the contents of the flask with water, allow to cool, rinse into a beaker, and determine the iron still remaining in the state of protochloride with chromate of potash (p. 198). Deduct this from the weight of the wire employed in the process; the difference expresses the quantity of iron which has been converted by the oxygen of the manganese from protochloride to sesquichloride.* This difference multiplied by $\frac{43 \cdot 5}{56}$ or 0·7768, gives the amount of binoxide in the analyzed ore. This method also, if carefully executed, gives very accurate results. If you determine the excess of protochloride of iron with permanganate, do not forget the remarks on page 198, note.

The main reason why this method is less suitable for industrial use than the first lies in the fact, that the analyst must work with much smaller quantities of substance. Hence to obtain results equally accurate with those yielded by A, far greater nicety in weighing and manipulating is required. Instead of metallic iron, weighed quantities of pure protosulphate of iron, or of sulphate of protoxide of iron and ammonia, may be used.

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* In very precise experiments, the weight of the iron must be multiplied by 0·997, since pianoforte wire may always be assumed to contain about 0·003 impurities.

III. Estimation of Moisture in Manganese.

§ 216.

In the purchase and sale of manganese, a certain proportion of moisture is usually assumed to be present, and often a percentage is fixed within which the moisture must be confined. In estimating the moisture the same temperature should be employed, at which the drying for the purpose of determining the binoxide is effected (§ 214, I.).

As the amount of moisture in an ore may be altered by the operations of crushing and pulverizing, the experiment should be made with a sample of the mineral which has not yet been subjected to these processes. The drying must be continued until no further diminution of weight is observed; at 100°, this takes about 6 hours, at 120°, generally only 1½ hours. If the moisture in a manganese ore is not to be estimated on the spot, but in the laboratory, a fair average sample of the ore should be forwarded to the chemist in a strong, perfectly dry, and well-corked bottle.

IV. Estimation of the Amount of Hydrochloric Acid required for the complete Decomposition of a Manganese.

§ 217.

Different manganese ores, containing the same amount of available oxygen, or, as it is usually expressed, of binoxide, may require very different quantities of hydrochloric acid to effect their decomposition and solution, so as to give an amount of chlorine corresponding to the available oxygen in them;—thus, an ore consisting of 60 per cent. of binoxide of manganese and 40 per cent. of sand and clay, requires 2 eq. hydrochloric acid to 1 eq. of available oxygen; whereas an equally rich ore containing lower oxides of manganese, sesquioxide of iron, or carbonate of lime requires a much larger proportion of hydrochloric acid.

The quantity of hydrochloric acid in question may be determined by the following process:—

Determine the strength of 10 c. c. of a moderately strong hydrochloric acid (of, say, 1·10 sp. gr.) by means of solution of sulphate of copper and ammonia (§ 205). Warm 10 c. c. of the same acid with a weighed quantity (about 1 grm.) of the manganese, in a small long-necked flask, with a glass tube, about 3 feet long, fitted into the neck. Fix the flask in a position that the tube is directed obliquely upwards, and then gently heat the contents. As soon as the manganese is decomposed, apply a somewhat stronger heat for a short time, to expel the chlorine which still remains in solution; but carefully avoid continuing the application of heat longer than is absolutely necessary, as it is of importance to guard against the slightest loss of hydrochloric acid. Let the flask cool, dilute the contents with water, and determine the free hydrochloric acid remaining by solution of sulphate of copper and ammonia. Deduct the quantity found from that originally added; the difference expresses the amount of hydrochloric acid required to effect the decomposition of the manganese ore.

7. ANALYSIS OF COMMON SALT.

§ 218.

I select this example to show how to analyse, with accuracy and tolerable expedition, salts which, with a predominant principal ingredient, contain small quantities of other substances.

a. Reduce the salt by trituration to a uniform powder, and put this into a stoppered bottle.

b. Weigh off 10 grm. of the powder, and dissolve in a beaker by digestion with water; filter the solution into a ½-litre flask, and thoroughly wash the small residue which generally remains. Finally, fill the flask with water up to the mark, and shake the fluid.

If small white grains of sulphate of lime are left on dissolving the salt, reduce them to powder in a mortar, add water, let the mixture digest for some time, decant the clear supernatant fluid on to a filter, triturate the undissolved deposit again, add water, &c., and repeat the operation until complete solution is effected.

c. Ignite and weigh the dried insoluble residue of *b*, and subject it to a qualitative examination, more especially with a view to ascertain whether it is perfectly free from sulphate of lime.

d. Of the solution *b*, measure off successively the following quantities:—

For	*e.*	50 c. c.	corresponding	to	1	grm.	of common	salt.
"	*f.*	150 c. c.	"	"	3	"	"	"
"	*g.*	150 c. c.	"	"	3	"	"	"
"	*h.*	50 c. c.	"	"	1	"	"	"

e. Determine in the 50 c. c. measured off, the *chlorine* as directed § 141, I., *a* or *b*.

f. Determine in the 150 c. c. measured off, the *sulphuric acid* as directed § 132, I., 1.

g. Determine in the 150 c. c. measured off, the *lime* and *magnesia* as directed p. 349, **29.**

h. Mix the 50 c. c. measured off, in a platinum dish, with about ½ c. c. of pure concentrated sulphuric acid, and proceed as directed § 98, 1. The neutral residue contains the sulphates of soda, lime, and magnesia. Deduct from this the quantity of the two latter substances as resulting from *g*; the remainder is sulphate of *soda*.

i. Determine in another weighed portion of the salt, the *water* as directed § 35, *a*, *α*, at the end.

k. Bromine and other bodies, of which only very minute traces are found in common salt, are determined by the methods described in Part I.

8. ANALYSIS OF GUNPOWDER.*

§ 219.

Gunpowder, as is well known, consists of nitre, sulphur, and charcoal, and, in the ordinary condition, invariably contains a small quantity of moisture. The analysis is frequently confined to the determination of the three constituents and the moisture, but often the examination is extended to the nature of the charcoal, and the carbon, hydrogen, oxygen, and ash therein are estimated.

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* As regards the determination of the sp. gr. of gunpowder, I refer to Heeren's paper on the subject, in Mittheilungen des Gewerbevereins für Hannover, 1856, 168—178; Polyt. Centralbl. 1856, 1118.

a. Determination of the Moisture.

Weigh 2—3 grm. of the substance (not reduced to powder) between two well-fitting watch-glasses, and dry in the desiccator, or at a gentle heat, not exceeding 60°, till the weight remains constant.

b. Determination of the Nitre.

Place an accurately weighed quantity (about 5 grm.) on a filter, moistened with water; saturate with water, and, after some time, repeatedly pour small quantities of hot water upon it until the nitrate of potassa is completely extracted. Receive the first filtrate in a small weighed platinum dish, the washings in a beaker or small flask. Evaporate the contents of the platinum dish cautiously, adding the washings from time to time, heat the residue cautiously to incipient fusion, and weigh it.*

c. Determination of the Sulphur.

Oxidize 2—3 grm. of the powder with pure concentrated nitric acid and chlorate of potash, the latter being added in small portions, while the fluid is maintained in gentle ebullition. If the operation is continued long enough, it usually happens that both the charcoal and sulphur are fully oxidized, and a clear solution is finally obtained. Evaporate with excess of pure hydrochloric acid on a water-bath to dryness, filter, if undissolved charcoal should render it necessary, and determine the sulphuric acid after § 132, I., 1.

d. Determination of the Charcoal.

Digest a weighed portion of the powder repeatedly with sulphide of ammonium, till all sulphur is dissolved, collect the charcoal on a filter dried at 100°, wash it first with water containing sulphide of ammonium, then with pure water, dry at 100°, and weigh.

The charcoal so obtained must, under all circumstances, be tested for sulphur by the method given under *c*, and if occasion require, the sulphur must be determined in an aliquot part. The charcoal may also be examined as regards its behavior to potash solution (in which "red charcoal"† is partially soluble) and an aliquot part may be subjected to elementary analysis according to § 178. For this latter purpose take a portion of the charcoal dried at 100°, and dry at 190° (WELTZIEN). If the charcoal, on this second drying, suffers a diminution of weight, calculate the latter into per-cents of the gunpowder, deduct it from the charcoal, and add it to the moisture.

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* The nitrate of potassa may also be estimated in an expeditious manner, and with sufficient accuracy for technical purposes, by means of a hydrometer, which is constructed to indicate the percentage of this ingredient when floated in water containing a certain proportion of gunpowder in solution. A method based upon the same principle, proposed by Uchatius, is given in the Wiener akad. Ber. X. 748; also Ann. d. Chem. und Pharm. 88, 395.

† Incompletely carbonized wood.

9. ANALYSIS OF NATIVE AND, MORE PARTICULARLY, OF MIXED SILICATES.*

§ 220.

The analysis of silicates which are completely decomposed by acids has been described in § 140, II., *a*; and that of silicates which are not decomposed by acids, in § 140, II., *b*. I have therefore here only to add a few remarks respecting the examination of mixed silicates, *i.e.*, of such as are composed of silicates of the two classes (phonolites, clay-slates, basalts, meteoric stones, &c.).

After the silicate has been very finely pulverized and dried at 100° it is usually treated for some time, at a gentle heat, with moderately concentrated hydrochloric acid, evaporated to dryness on the water-bath, the residue moistened with hydrochloric acid, water added, and the solution filtered; it is often preferable, however, to digest the powder with dilute hydrochloric acid (of about 15 per cent.) for some days at a gentle heat, and then at once filter the solution. Which of the two ways it is advisable to adopt, and indeed whether the method here described (which was first employed by CHR. GMELIN in the analysis of phonolites), may be resorted to, depends upon the nature of the mixed minerals. The more readily decomposable the one of the constituent parts of the mixture is, and the less readily decomposable the other, the more constant the proportion between the undissolved and the dissolved part is found to remain in different experiments; in other words, the less the undissolved part is affected by further treatment with hydrochloric acid, the more safely may this method of decomposition be resorted to.

The process gives:—

a. A *hydrochloric acid solution*, containing, besides a little silicic acid, the bases of the decomposed silicate in the form of metallic chlorides, which are separated and determined by the proper methods.

b. An *insoluble residue*, which contains, besides the undecomposed silicate, the separated silicic acid of the decomposed silicate.

After the latter has been well washed with water, to which a few drops of hydrochloric acid have been added, transfer it, still moist, in small portions at a time, to a boiling solution of carbonate of soda (free from silicic acid) contained in a platinum dish; boil for some time, and filter off each time, still very hot, through a weighed filter. Finally, rinse the last particles of the residue which still adhere to the filter completely into the dish, and proceed as before. Should this operation not fully succeed, dry and incinerate the filter, transfer the ash to the platinum dish, and boil repeatedly with the solution of carbonate of soda till a few drops of the fluid finally passing through the filter remain clear on warming with excess of chloride of ammonium. Wash the residue, first with hot water, then—to insure the removal of every trace of carbonate of soda which may still adhere to it—with water slightly acidified with hydrochloric acid, and finally again with pure water. Collect the washings in a separate vessel (H. ROSE).

Acidify the alkaline filtrate with hydrochloric acid, and determine in it the silicic acid which belongs to the silicate decomposed by hydrochloric acid, as directed § 140, II., *a*. Dry the undissolved silicate at

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* Comp. Qual. Anal. §§ 205–208. The quantitative analysis must always be preceded by a minute and comprehensive qualitative analysis.

100°, and weigh. The difference gives the quantity of the dissolved silicate. Treat the undissolved silicate exactly as directed § 140, II., *b*.

Silicates dried at 100° occasionally contain *water*. This is determined by taking a weighed portion of the mixed silicate dried at 100° and igniting in a platinum crucible, or—in presence of carbon or protoxide of iron—in a tube, through which a stream of dry air is drawn, the moisture expelled from the substance being retained by a weighed chloride of calcium tube. To ascertain whether the water thus expelled proceeds from the silicate decomposable by hydrochloric acid, or from that which hydrochloric acid fails to decompose, a sample of the latter, dried at 100°, is also ignited in the same manner. Suppose, for instance, the mixed silicate under examination consists of 50 per cent. of silicate decomposed by hydrochloric acid, and 50 per cent. of silicate which hydrochloric acid fails to decompose; and that the latter contains 47 parts of anhydrous substance, and 3 parts of water; the determination of the water would give, for the mixed silicate 3 per cent., for the portion not decomposed by hydrochloric acid 6 per cent. Now, as 3 bears the same proportion to 6 as the undecomposed silicate (50 per cent.) bears to the mixed silicate (100 per cent.), it is clear that the silicate decomposed by hydrochloric acid gives no water upon ignition.

If the escaping aqueous vapors manifest acid reaction, owing to disengagement of *hydrochloric acid* or *fluoride of silicon*, mix the substance with 6 parts of finely triturated recently ignited oxide of lead in a small retort, weigh, ignite, and weigh again. If the water passing over still manifests acid reaction, connect the retort with a small receiver containing water, and determine the hydrofluosilicic acid in the latter, after the termination of the process. According to SAINTE-CLAIRE DEVILLE and FOUQUÉ,[*] by properly conducting the ignition the water may usually be expelled free from combinations of fluorine, since the latter require a far higher temperature for expulsion than the former requires. After the water has been driven off the fluorine is then expelled by stronger ignition, either as alkaline metallic fluoride or as fluoride of silicon.

The undecomposed part of a mixed silicate occasionally contains *carbonaceous organic matter*, in which case it is the safest way to treat an aliquot part of it in a current of oxygen gas, and weigh the carbonic acid produced (§ 178). According to DELESSE, traces of nitrogen are almost invariably present in the organic matter contained in silicates.

Silicates often contain admixtures of other minerals (magnetite, pyrites, apatite, carbonate of lime, &c.) which may sometimes be detected by the naked eye or with the aid of a magnifying glass. It would be rather a difficult undertaking to devise a generally applicable method for cases of this description; I therefore simply remark that it is occasionally found advantageous to treat the substance first with acetic acid, before subjecting it to the action of hydrochloric acid; this will more especially effect, without the least difficulty, the separation of the carbonates of the alkaline earths. As examples of complete examinations of this kind I may cite some analyses by DOLLFUSS and NEUBAUER,[†] which were made in my laboratory.

If *sulphides* are present, determine the sulphur by one of the methods given § 148, II., *A*.* As regards the methods in the wet way, it must be borne in mind, that when baryta, strontia, or lead is present, a portion of the sulphuric acid produced remains in the insoluble residue; on fusion with alkaline carbonate and nitrate this is not the case. If, besides sulphide, a *sulphate* is present, determine the sulphuric acid of the latter, by boiling a separate portion of the substance with a solution of carbonate of potash or soda for a long time, filtering, acidifying the filtrate, and precipitating with chloride of barium. The sulphuric acid thus obtained is deducted from the quantity obtained after treatment with oxidizing agents, and the remainder corresponds with the sulphur in the sulphide.

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[*] Compt. rend. 38, 317; Journ. f. prakt. Chem. 62, 78.

[†] Journ. f. prakt. Chem. 65, 199.

The *protoxide of iron* may be conveniently determined by Cooke's process (p. 369).

If silicates contain small quantities of *titanic acid*, as is very frequently the case, care must be taken not to overlook this admixture. If the silicic acid has been separated by evaporation with hydrochloric acid—whether preceded or not by decomposition with carbonated alkali—and the evaporation has been effected on the water-bath, and the dry mass has been treated with a sufficient quantity of hydrochloric acid, the titanic acid, or at least by far the greater part of it, is found in the hydrochloric acid solution.

The separated silica may be tested for titanic acid, as follows:—Treat in a platinum dish with hydrofluoric acid and a little sulphuric acid, evaporate, fuse the residue with bisulphate of potash, dissolve in cold water, filter if necessary, and separate the titanic acid from the sulphuric acid solution by the method given § 107.

As regards the titanic acid contained in the hydrochloric acid solution filtered from the silicic acid, it is precipitated with the sesquioxide of iron and alumina, when ammonia is added (§ 161, 3). In this precipitate it may be determined either (*a*) by igniting the precipitate in hydrogen, extracting the reduced iron by digestion with dilute hydrochloric acid, fusing the residue with bisulphate of potash, taking up with cold water, and precipitating the titanic acid by boiling (§ 107) or (*b*) by fusing the precipitate at once with bisulphate of potash, dissolving in cold water, neutralizing the solution as nearly as possible with carbonate of soda, diluting with water, so that not more than 0·1 grm. of the oxides may be contained in 50 c. c., adding to the cold solution hyposulphite of soda in slight excess, waiting till the fluid, which was at first violet, has become quite colorless, and consequently the whole of the sesquioxide of iron is reduced, boiling till sulphurous acid ceases to be disengaged, filtering, washing the precipitate with boiling water, drying, gently igniting in a covered porcelain crucible, to expel sulphur, then taking the lid off and increasing the heat; we thus obtain the alumina (CHANCEL†) and the titanic acid (A. STROMEYER‡) together, free from sesquioxide of iron; they are separated by the method above given.

10. ANALYSIS OF LIMESTONES, DOLOMITES, MARLS, &c.

As the minerals containing carbonate of lime and carbonate of magnesia play a very important part in manufactures and agriculture, the chemist is often called upon to analyze them. The analytical process differs according to the different object in view. For technical purposes, it is sufficient to determine the principal constituents; the geologist takes an interest also in the matter present in smaller proportions; whilst the agricultural chemist seeks a knowledge not only of the constituents, but also of the state of solubility, in different menstrua, in which they are severally present.

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* The methods in the wet way would as a rule be preferable.

† Compt. rend. 46, 987; Annal. d. Chem. u. Pharm. 108, 237.

‡ Annal. d. Chem. u. Pharm. 113, 127.

I will give, in the first place, a process for effecting a complete and accurate analysis; and, in the second place, the volumetric methods by which the carbonate of lime (and the carbonate of magnesia) may be determined. An accurate qualitative examination should always precede the quantitative analysis.

A. METHOD OF EFFECTING THE COMPLETE ANALYSIS.

§ 221.

a. Reduce a large piece of the mineral to powder, mix this uniformly, and dry at 100°.

b. Treat about 2 grm., in a covered beaker, with dilute hydrochloric acid in excess, evaporate to dryness in a platinum or porcelain dish, moisten the residue with hydrochloric acid, heat with water, filter on a dried and weighed filter, wash the insoluble residue, dry at 100°, and weigh. It generally consists of separated *silicic acid*, *clay*, and *sand*: but it often contains also *humus-like matter*. Opportunity will be afforded in *g* for examining this residue.

c. Mix the hydrochloric acid solution with chlorine water, then with ammonia in slight excess, and let the mixture stand at rest for some time, in a covered vessel, at a gentle heat. Filter off the precipitate, which contains—besides the hydrates of sesquioxide of iron, sesquioxide of manganese, and alumina—the phosphoric acid which the analyzed compound may contain, and, moreover, invariably traces of lime and magnesia; wash slightly, and redissolve in hydrochloric acid; heat the solution, add chlorine water, and then precipitate again with ammonia; filter off the precipitate, wash, dry, ignite, and weigh.

For the estimation of the several components of the precipitates, viz., *sesquioxide of iron*, *protosesquioxide of manganese*, *alumina*, and *phosphoric acid*, opportunity will be afforded in *g*.

d. Unite the fluids filtered from the first and second precipitates produced by ammonia, and determine the *lime* and *magnesia* as directed § 154, 6 (**29**).

e. If the limestone dried at 100° still gives *water* upon ignition, this is estimated best as directed § 36.

f. If the limestone contains no other volatile constituents besides water and carbonic acid, ignite with fused borax (p. 288, *c*), and subtract from the loss of weight suffered, the water found in *e*; the difference is the *carbonic acid*. If this method is inapplicable, determine the carbonic acid as directed p. 290, *bb*, or 291, *cc*, or as on p. 293, *e*.

g. To effect the estimation of the constituents present in smaller proportion, as well as the analysis of the residue insoluble in hydrochloric acid, and of the precipitate produced by ammonia, dissolve 20—50 grm. of the mineral in hydrochloric acid. As the evaporation to dryness of large quantities of fluid is always a tedious operation, gently heat the solution for some time, to expel the carbonic acid; then filter through a weighed filter into a litre flask, wash the residue, dry, and weigh it. (The weight will not quite agree with that of the residue in *b*, as the latter contains also that part of the silicic acid which here still remains in solution.)

a. Analysis of the insoluble Residue.

aa. Treat a portion with boiling solution of pure carbonate of soda (§ 220, *b*), and separate the silicic acid from the solution (§ 140, II., *a*); this process gives the quantity of that portion of the *silicic acid* contained in the residue, which is *soluble in alkalies.*

bb. Treat another portion, by the usual process for silicates (§ 140, II., *b*), and deduct from the *silicic acid* found, the amount obtained in *aa.*

cc. If the residue contains *organic matter* (humus), determine, in a portion, the carbon by the method of ultimate analysis (p. 430, *b*). PETZHOLDT,[*] who determined by this method the coloring organic matter of several dolomites, assumes that 58 parts of carbon correspond to 100 parts of organic substance (humic acid).

dd. If the residue contains *pyrites*,[†] fuse another portion of it with carbonate of soda and nitrate of potassa; macerate in water, add hydrochloric acid, evaporate to dryness, moisten with hydrochloric acid, gently heat with water, filter, determine the sulphuric acid in the filtrate, and calculate from the result the amount of pyrites present.[‡]

β. Analysis of the Hydrochloric Acid Solution.

Make the solution up to 1 litre.

aa. For the determination of the *silicic acid* that has passed into solution, and of the *baryta, strontia, alumina, manganese, iron,* and *phosphoric acid,* evaporate 500 c. c., and dry the residue at 100—110°. Treat the dry mass, in order to separate silicic acid, &c. (precipitate I.), with hydrochloric acid and water, boil the solution with nitric acid, add ammonia, boil till the excess of ammonia has escaped, filter, wash slightly, dissolve on the filter with hydrochloric acid, reprecipitate in the same manner with ammonia, and filter off precipitate II., which contains sesquioxide of iron, &c. Digest the united filtrates in a nearly filled and closed flask with sulphide of ammonium in a slightly warm place for 24 hours, then filter off precipitate III. This consists principally of sulphide of manganese; it is to be washed with water containing sulphide of ammonium. Precipitate the filtrate with carbonate of ammonia and ammonia, allow to stand 24 hours, and then filter off precipitate IV., which consists for the most part of carbonate of lime, and is to be washed with water containing ammonia. Evaporate the filtrate in a porcelain dish to dryness, project the residue, little by little, into a red hot platinum dish, drive off the ammonia salts, moisten the residue with hydrochloric acid, dissolve it in water, and boil, with addition of pure milk of lime, to strongly alkaline reaction. Filter off precipitate V., which is composed of magnesia and the excess of lime, wash it, precipitate the filtrate with carbonate of ammonia and ammonia, and, after long standing, filter off precipitate VI., which is to be washed with water containing ammonia.

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[*] Journ. f. prakt. Chem. 63, 194.

[†] Compare Petzholdt, *loc cit.*; Ebelmen (Compt. rend. 33, 681); Deville (Compt. rend. 37, 1001; Journ. f. prakt. Chem. 62, 81); Roth (Journ. f. prakt. Chem. 58, 84).

[‡] If the residue contains sulphate of baryta or strontia, these compounds are formed again upon evaporating the soaked mass with hydrochloric acid; they remain accordingly on the filter, whilst the sulphuric acid formed by the sulphur of the pyrites passes into the filtrate.

Precipitate I. consists principally of silicic acid. It may also contain sulphates of baryta and strontia. Treat it in a platinum dish with hydrofluoric acid and a little sulphuric acid, evaporate to dryness, and, if necessary, repeat this operation. Should a residue remain, fuse it with a small quantity of carbonate of soda, treat with water, filter, wash, dissolve in hydrochloric acid, and precipitate the solution with sulphuric acid. When the precipitate has settled filter it from solution *a*, and wash. Stop up the tube of the funnel, and fill the latter with solution of carbonate of ammonia, allow to stand 12 hours, open the funnel tube, wash the residue first with water, then with hydrochloric acid (solution *b*), finally again with water, and then weigh the pure residual sulphate of *baryta*. Mix the united solutions *a* and *b* with carbonate of ammonia and ammonia, allow to stand some time; if a precipitate forms (which may contain carbonate of strontia) filter it off, dry, and add to precipitate IV.

Precipitate II. consists principally of sesquioxide of iron; it contains also the alumina, and, provided there is enough iron, the whole of the phosphoric acid. Dissolve in hydrochloric acid, add pure tartaric acid, and then ammonia. Having fully convinced yourself that no precipitate is formed, precipitate the iron with sulphide of ammonium in a small flask, which must be nearly filled and closed, allow to stand till the fluid appears of a pure yellow color, filter, wash with water containing sulphide of ammonium, and determine the *iron* after § 113, 2. To the filtrate add a little pure carbonate of soda and pure nitrate of potassa, evaporate to dryness, and ignite till the residue is white. Add water and hydrochloric acid till the whole is dissolved,* and precipitate the clear fluid with ammonia. If a precipitate forms (alumina or phosphate of alumina, or a mixture of both), filter it off, and weigh. Mix the filtrate with a little sulphate of magnesia. If another precipitate forms, this time consisting of ammonio-*phosphate* of magnesia (which is to be determined after § 134, I., *b*. α) the alumina precipitate may be calculated as *phosphate of alumina* ($Al_2 O_3, P O_5$). If, on the contrary, no precipitate is formed, the phosphoric acid must be determined in the alumina precipitate as directed § 134, I., *b*, β.

Precipitate III. consists principally of sulphide of manganese. It may also contain traces of sulphides of nickel, cobalt, and zinc, carbonate of lime, &c. Treat with moderately dilute acetic acid, heat the filtrate, to remove any carbonic acid, add ammonia, precipitate with sulphide of ammonium, allow to stand 24 hours, and determine the *manganese* as protosulphide (§ 109, 2). If any residue was left insoluble in acetic acid, test it for the above-mentioned metals. The fluid filtered from the pure sulphide of manganese is to be mixed with carbonate of ammonia. If a precipitate forms it is to be treated with precipitate IV.

Precipitates IV. V. VI. The united mass of these precipitates, together with the small portions of alkaline earthy carbonates obtained during the treatment of precipitates I. and III. contain the whole of the strontia and the whole of the baryta which originally passed into the hydrochloric acid solution. Ignite the dried precipitate (if necessary in portions) in a platinum crucible, most intensely over the gas blowpipe. By this means any carbonates of baryta and strontia are converted into the caustic state, and a part, at all events, of the carbonate of lime into lime (ENGELBACH *). Boil the residue 5 or 6 times with small portions of water, pouring off the solution through a filter; neutralise the solution with hydrochloric acid, evaporate to dryness, and test a minute portion with the spectroscope—this minute portion is afterwards added to the rest. If *strontia* and lime alone are present, separate according to **28.** If baryta is present, separate the three alkaline earths after **24.**

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* I may remind the operator that the residue, which contains nitric acid, cannot be heated with hydrochloric acid in a platinum dish.

bb. Although it is possible in *aa* to test for metals precipitable by sulphuretted hydrogen from acid solution, *e.g.*, copper, and if required to determine them, still it is more convenient to employ a fresh quarter of the hydrochloric acid solution for this purpose. The precipitate obtained by passing the gas into the warm dilute solution is washed, dried, and treated with bisulphide of carbon. If a residue remains it is to be examined.

cc. The remaining quarter of the dilute hydrochloric acid solution is used for the estimation of the *alkalies.*† Mix with chlorine water, then with ammonia and carbonate of ammonia; after allowing the mixture to stand for some time, filter off the precipitate, evaporate the filtrate to dryness, ignite the residue in a platinum dish to remove the ammonia salts, and finally separate the magnesia from the alkalies as directed p. 345, **15.** The reagents must be most carefully tested for fixed alkalies, and the use of glass and porcelain vessels avoided as far as practicable.

Should the limestone contain a sulphate soluble in hydrochloric acid, precipitate the sulphuric acid by a small excess of chloride of barium, allow to settle, and filter off the sulphate of baryta (which is to be determined in the usual manner) before proceeding as above to the estimation of the alkalies.

d. As calcite and aragonite may contain *fluorides* (JENZSCH ‡), the possible presence of fluorine must not be disregarded in accurate analyses of limestones. Treat, therefore, a larger sample of the mineral with acetic acid until the carbonate of lime and carbonate of magnesia are decomposed; evaporate to dryness until the excess of acetic acid is completely expelled, and extract the residue with water (§ 138, I.). We have the fluorine in the residue. If it can be distinctly detected in a portion of the same,‖ the determination may be attempted after § 166, 5.

e. If the limestone under examination contains *chlorides*, treat a large sample with water and nitric acid, at a very gentle heat; filter, and precipitate the chlorine from the filtrate by solution of nitrate of silver.

f. It is often interesting for agriculturists to know the degree of solubility of a sample of limestone or marl in the weaker solvents. This may be ascertained by treating the sample first with water, then with acetic acid, finally with hydrochloric acid, and examining each solution and the residue. The analyses of marls made by C. STRUCKMANN[*] were done in this manner.

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* Zeitschrift f. analyt. Chem. 1, 474.

† The simplest way of ascertaining whether and what alkalies are present in a limestone, is the process given by Engelbach (Annal. d. Chem. u. Pharm. 123, [illegible]), viz., ignite a portion of the triturated mineral strongly in a platinum crucible over the blast, boil with a little water, filter, neutralize with hydrochloric acid, precipitate with ammonia and carbonate of ammonia, filter, evaporate the filtrate to dryness and examine with the spectroscope. The carbonate of ammonia precipitate may be evaporated with hydrochloric acid to dryness, and examined in like manner for baryta and strontia.

‡ Pogg. Annal. 96, 145.

‖ See Qual. Anal. § 146, 6.

l. To effect the separation of the caustic or carbonated lime, in hydraulic limes, from the silicates, DEVILLE[†] proposed to boil with solution of nitrate of ammonia, which he stated would dissolve the caustic lime and carbonate of lime, without exercising a decomposing action on the silicates. GUNNING[‡] found, however, that by this process the double silicates of alumina and lime are more or less decomposed, with separation of silicic acid. As yet no method is known by which the object here stated can be accomplished with absolute accuracy; the best way, perhaps, is treating the sample with dilute acetic acid; C. KNAUSZ[‖] recommends hydrochloric acid.

B. VOLUMETRIC DETERMINATION OF CARBONATE OF LIME AND CARBONATE OF MAGNESIA (for technical purposes).

§ 222.

a. If a mineral contains only carbonate of lime, the amount of the latter may be estimated from the quantity of acid required to effect its decomposition, the method described in § 210 being employed for the purpose. Or the carbonic acid in the mineral may be determined, say by the method described p. 291, *cc*, and 1 eq. carbonate of lime = 50 calculated for each eq. carbonic acid = 22.

b. But if the mineral contains, besides carbonate of lime, also carbonate of magnesia, the results obtained by either process give the quantity of carbonate of lime + carbonate of magnesia, the latter being expressed by its equivalent quantity of carbonate of lime (*i.e.*, 50 of carbonate of lime for 42 of carbonate of magnesia). If, therefore, you desire to know the actual amount of each, you must, in addition to the above determination, estimate one of the earths separately. For this purpose one of the two following methods may be employed:—

1. Mix the dilute solution of 2—5 grm. of the mineral with ammonia and oxalate of ammonia in excess, allow to stand for 12 hours and then filter. Ignite the precipitate of oxalate of lime, together with the filter, and treat the carbonate of lime produced as directed § 210. This process gives the amount of lime contained in the analyzed mineral; the difference between this and the former result gives the carbonate of lime which is equivalent to the amount of carbonate of magnesia present. To obtain perfectly accurate results by this method, repeated precipitation is indispensable (see § 154, 6, *a*).

2. Dissolve 2—5 grm. of the mineral in the least possible excess of hydrochloric acid, and add a solution of lime in sugar water as long as a precipitate forms. By this operation the magnesia only is precipitated. Filter, wash, and treat the precipitate as directed § 210; the result represents the quantity of the magnesia. Deduct the quantity of car-

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[*] Annal. d. Chem. u. Pharm. 74, 170.

[†] Compt. rend. 37, 1001; Journ. f. prakt. Chem. 62, 81.

[‡] Journ. f. prakt. Chem. 62, 318.

[‖] Gewerbeblatt aus Würtemberg, 1855, Nr. 4; Chem. Centralbl., 1855, 244.

[illegible] of the tota [illegible] of carbonate of lime pre

[illegible] proportion of magnesi

[illegible] ANALYSIS OF IRON ORES.

§ [illegible].

[illegible], a sample of 3—10 grm. is finely pulve [illegible] in a tightly stoppered bottl

A. [illegible] OF IRON.

[illegible]. In case of spathic iron and hydrous hematites, [illegible] may be dissolved in strong hydrochloric acid with aid o [illegible]. In presence of protoxide of iron, sulphides, or organi [illegible], and heat until these substances are oxidi [illegible] sulphuric acid in excess, and evaporate until [illegible]. A residue of silica may be disregarded, unles [illegible] interfere with accurate division of the solu [illegible] it must be filtered off. Dilute to 100 c. c. If t [illegible] insoluble in hydrochloric acid, it is best to m [illegible] weight of carbonate of soda (if sulphides or organ [illegible] be present, [illegible] in a porcelain crucible before mixing [illegible] or add to the mixture a suitable proportion—$\frac{1}{10}$—of pulveri [illegible] and fuse for 15 minutes. Dissolve the fused mass with a sma [illegible] sulphuric acid (1 volume of acid to 4 volumes of water [illegible] was employed, or silica is present in the fusion, evaporate unt [illegible] of sulphuric acid arise, and dilute to 100 c. c.

Determination of the iron is made volumetrically, on portions [illegible] with permanganate of potassa after previous reduction [illegible] of zinc, or directly by standard solution of hyposulphite of sod

In presence of titanium the latter method must be employed [illegible] acid is partially reduced by zinc, as shown by the purpl [illegible] the solution.

B. ESTIMATION OF IRON, MANGANESE, SILICA, AND PHOSPHOR

The ore (2 grm.) is fluxed with carbonate of soda as describ dissolved in dilute sulphuric acid, evaporated and heated until sulphuric acid begin to appear, treated with water, and filtered silica. The filtrate is diluted or concentrated to 200 c. c. and estimated in portions of 25 c. c., by hyposulphite, p. 203. F c. c. the iron is thrown down by acetate of soda, p. 123, *e*.

Manganese is estimated in the filtrate by precipitation with p. [illegible], *d*, and if the quantity be large, by subsequent conver pyrophosphate. The operator must not omit to satisfy himsel complete separation of manganese, by testing the clear liquid o with bromine and warming. If the solution is or becomes acid, nearly neutralize it with carbonate of soda before add mine. The final filtrate from the bromine precipitates should tralized with ammonia and tested with sulphide of ammonium, in order to be certain of the complete precipitation of mangane

Phosphoric acid, if present, exists in the precipitate by acetate of soda. This is dissolved in nitric acid, diluted to 200 c. c., and precipitated by means of molybdenum solution. The phosphoric acid is weighed as pyrophosphate of magnesia. The directions found on p. 271 must be strictly followed. If arsenic acid be present, this must be removed by passing sulphuretted hydrogen at 70° through the sulphuric solution, which, after removal of the sulphide of arsenic, must be heated with nitric acid to peroxidize the iron.

C. Estimation of Sulphur.

In presence of pyrites fuse the ore (1—3 grm.) with thrice its weight of carbonate of soda and nitre, both free from sulphur, in a porcelain dish, acidulate with hydrochloric acid, evaporate to dryness over the water-bath to separate silica, and precipitate with chloride of barium. To purify the $BaO\ SO_3$, when yellow from presence of iron, fuse it with carbonate of soda, extract the fused mass with water, acidulate the aqueous solution (filtered off from $Fe_2\ O_3$ and $BaO\ CO_2$) with hydrochloric acid, and precipitate again with chloride of barium.

D. Estimation of Titanium.

Titanium is estimated in 1—5 grm. of ore, which should be fused with soda, the fused mass dissolved in excess of sulphuric acid, evaporated to dryness cautiously in an air-bath, the heat being gradually raised until the bisulphate of soda formed passes into fusion at a low red heat. Cover the *cold* mass with cold water, let stand a number of hours until it is thoroughly softened and dissolved, dilute to 500—700 c. c., filter off from silica, add bisulphite of soda to reduce the iron to protoxide, heat to boiling for an hour or more, replacing the evaporated water, and adding bisulphite of soda, or solution of sulphurous acid, from time to time. The titanic acid is then thrown down completely, provided too much free sulphuric acid be not present. Filter and wash with hot water. To the filtrate and washings add more sulphurous acid, or sulphite, and if strongly acid nearly neutralize with carbonate of soda, and boil for thirty minutes longer; filter off any additional precipitate, and repeat the operation as long as titanic acid separates. Test 100 c. c. of the last filtrate by concentrating with sulphuric acid and zinc, to be certain that all titanic acid is precipitated. The impure titanic acid thus obtained is ignited and weighed, see p. 178. It is then redissolved by fusion with bisulphate of soda, and treatment with cold water, and either reprecipitated by boiling its solution, mixed with sulphurous acid as before, in order to obtain it free from iron, or the iron may be determined volumetrically in the solution by means of hyposulphite of soda, p. 203, 3, *b*, and the titanic acid estimated by difference.]

12. Assay of Copper Ores.*

§ 224.

A. Mohr's *Method for Oxides, Silicates, and Carbonates of Copper.*

Powder the ore finely; if rich, take 1 grm., if poor, 3 grm. Treat in a porcelain dish of 10 cm. diameter with some sulphuric acid, water, and nitric acid, cover the dish with a large watch-glass and heat to boiling. As soon as the mass is nearly dry and ceases to spirt, remove the watch-glass and increase the flame, maintaining an elevated temperature till no more fumes escape; allow to cool, add distilled water, heat to boiling, filter into a small platinum dish, wash with hot water, evaporate the washings and transfer them also to the platinum dish, and finally—having made quite sure that the residue insoluble in water gives up no copper to acids—precipitate the copper with zinc, after p. 229, 2, *a*. The light-red color of the copper is an indication of its purity. It will be seen that we have in view in this process the removal, as far as possible, of the metals precipitable by zinc, viz.: lead, antimony, and tin. [Arsenic is not fully removed, and in this, as in the following processes, must be separated by sulphide of sodium. **128**, p. 329.]

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* See also Steinbeck's Method, Chemical News, v. 19, p. 207, and Luckow's Method, idem. p. 221.

[B. GIBBS' *Method for Sulphides*.*

Mix the finely pulverized ore in a porcelain crucible with 3—4 times its weight of a mixture of 10 parts of nitre, and 14 parts of bisulphate of potash. Heat the whole slowly to low redness—best in a muffle. The sulphides are completely oxidised without frothing. Add enough sulphuric acid to convert all the sulphate of potash into bisulphate, and heat again carefully until the contents of the crucible fuse to a clear mass. Dissolve in water, filter from silica, etc., and precipitate the copper as described p. 229, *b*.]

[C. STORER AND PEARSON'S *Method for Sulphides*.†

The ore, 2—5 grm., is pulverized and mixed with its bulk of powdered chlorate of potash in a porcelain dish, and covered with a watch-glass or inverted funnel; add nitric acid of ordinary strength, rather more than would be sufficient to cover the powder. Heat to gentle ebullition, adding from time to time chlorate of potash, if needful, until the sulphur is completely oxidized. Rinse the cover into a separate beaker. When the contents of the porcelain dish are cold, add a quantity of strong hydrochloric acid, rather larger than the quantity of nitric acid first employed; evaporate the whole to dryness, to render silica insoluble. Treat the residue with water, and mix the whole with the rinsings. Heat the liquid nearly to boiling, and add strong solution of protosulphate of iron, slightly acidulated with sulphuric acid; keep the whole hot until the contents of the beaker become almost black, and no more gas is disengaged.

When the nitric acid has been reduced by this treatment, filter into a wide beaker and precipitate by a clean sheet of iron, or by a flat coil of iron wire. Wash the metallic copper with water, then with alcohol, and, if need be, ignite it in a current of hydrogen before weighing.‡]

[* Am. Journ. Sci., xliv. 212.]

† Am. Journ. Sci., xlviii. 194.]

‡ The precipitation by iron succeeds well when iron can be obtained which dissolves in dilute acid without the separation of black particles or flakes in weighable quantity. If the copper solution be cold, dilute, and nearly neutral when the iron is first placed in it, the copper has little adhesion to the iron, and may be readily detached from it for the purpose of weighing. If, as soon as the iron is coated with copper, hydrochloric acid (30 c. c.) be added, and the whole be heated to near the boiling-point, and maintained at that temperature, but without ebullition, the residue of the copper is deposited as a spongy coherent mass, which,

13. Analysis of Galena.

§ 225.

This is the most widely spread of the lead ores. It frequently contains larger or smaller quantities of iron, copper, and silver, occasionally traces of gold, and commonly also more or less gangue, insoluble in acids.

Reduce the ore to a fine powder, and dry at 100°.

Oxidize a weighed quantity (1—2 grm.) with highly concentrated red fuming nitric acid, free from chlorine and sulphuric acid (see p. 326). For this purpose use a capacious flask, covered during the operation with a watch-glass; do not put the tube in which the powder was weighed into the flask. If the acid is sufficiently strong, the sulphur will be fully oxidized. After you have warmed gently for a long time, add 3 or 4 c. c. pure concentrated sulphuric acid, which you have previously diluted with a little water, and heat on an iron plate, till all the nitric acid is evaporated. Dilute with water, filter, wash the residue with water containing sulphuric acid, and displace the latter with alcohol. Collect the alcoholic washings separately.

a. Dry the *residue*, ignite, and weigh (§ 116, 3). It consists of sulphate of lead, gangue undecomposed by the acid, silicic acid, &c. Heat the whole, or a fractional part, with hydrochloric acid to boiling; let the insoluble matter subside, and then decant the supernatant clear liquid on to a filter; pour a fresh portion of hydrochloric acid on the residue, boil again, allow to subside, and decant, and repeat this operation until the sulphate of lead is completely dissolved; finally, place the residue on the filter, and wash with boiling water until every trace of chloride of lead is removed; dry, ignite, and weigh the *residue*. Subtract the weight found from that of the original residue: the difference expresses the quantity of sulphate of *lead* which the latter contained. Instead of using hydrochloric acid, the sulphate of lead may also be dissolved by heating with an aqueous solution of tartrate or acetate of ammonia and caustic ammonia; or it may be first converted into carbonate of lead, by digestion with solution of carbonate of soda, washed and dissolved in dilute nitric acid.

b. The *sulphuric acid solution* is free from any weighable trace of lead, if the process has been properly conducted. It contains the metals present in the ore in addition to lead. First add some hydrochloric acid, to precipitate the *silver*, if present. If a turbidity or precipitate is formed, keep the fluid for some time in a warm place, till the chloride of silver has subsided. The latter is filtered off and may be determined after § 115, 1. In the case of very small quantities, I prefer to incinerate the filter with the precipitate in a porcelain crucible, to ignite the residue for a short time in hydrogen, to dissolve the trace of metallic silver in nitric acid, to evaporate the solution in the crucible to dryness, to take up the residue with water, and to estimate the silver in the solution by Pisani's method (p. 215).

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with care, may be removed from the iron and washed without falling to pieces or oxidizing (see p. 229, 2, *a*, for details of washing). If the copper should be difficult to collect by decantation, it may be gathered on a small filter, and, after burning, the latter may be either reduced by hydrogen or calcined to oxide (p. 229, bottom).]

Precipitate the fluid filtered from the chloride of silver with sulphuretted hydrogen. The precipitate generally contains a little *sulphide of copper*, occasionally also other *sulphides*. Separate these, as well as the metals in the filtrate, which are precipitable by sulphide of ammonium (*iron*, *zinc*, &c.), according to the methods of Section V.

The foregoing method does not enable the assayer to determine very small quantities of silver* and the trifling traces of gold which, according to PERCY and SMITH,† are often found in galena. To effect this, it is, in the first place, necessary to produce a button containing the whole or part of the lead of the galena, and the whole of the silver and gold, and then to separate the latter metals. This is accomplished as described in § 226 and § 227.

[For the estimation of the *sulphur*, take a fresh portion of the pulverized ore and bring it into solution by method C, p. 526, filter from silica, in presence of iron, add a lump of solid tartaric acid, precipitate hot by chloride of barium, and wash by decantation first with hot water, and finally with dilute solution of acetate of ammonia. The tartaric acid prevents precipitation of iron, the acetate of ammonia purifies the precipitate from alkali and baryta salts.—STORER and PEARSON.‡]

[14. SILVER ASSAY.

§ 226.

Assay by Scorification and Cupellation.

A. ORES POOR IN SILVER.

1. *Preparation of the Ore.* The well-sampled ore is pulverized and passed through a sieve with 60 to 80 holes to the linear inch. If particles of metallic silver or malleable ore remain upon the sieve, they must be assayed separately.

The fluxes required are, 1, *Assay lead*, prepared by shaking melted lead in a wooden box and sifting through meshes of $\frac{1}{16}$ inch; 2, *Borax* or *borax-glass;* and 3, *Quartz sand* or *powdered glass*, to form silicates with the metallic and earthy oxides, and also sometimes to prevent the oxide of lead from destroying the scorifier. The proportions of the fluxes vary with different ores, and should be sufficient to form a liquid slag and a lead button of convenient size. The addition of too much borax will envelop the metallic lead before sufficient oxide of lead is formed to decompose the silver compounds.

Galena requires 6 parts lead and no borax; quartzose ores about 8 parts and no borax; blende, mispickel, and pyrites about 16 parts, and $\frac{1}{4}$ to 1 part borax; copper and tin compounds 20 to 30 of lead, and nickel and cobalt even more; *nickelspeise* 16 parts of lead and repeated scorifications; ores containing calcite, dolomite, barytes, or fluorspar, 8 parts of lead and 12 parts borax or glass. In case of doubt as to the nature of the ore, begin with 8 parts of lead, and, if the fusion is not good, repeat with a larger proportion of lead.

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[*] Argentiferous galenas generally contain only between 0·03 to 0·18, rarely above 0·5% silver; and a great many contain far less than 0·03%.

[†] Phil. Mag., VII. 126.

[‡] Am. Jour. Sci., XLVIII. 193.

2. *Scorification.* The objects of this process are to concentrate all the silver in a lead button, to decompose the sulphides, etc., and to dissolve and slag off earthy and other substances by means of the oxide of lead formed.

In this process all the sulphur of the heavy metallic sulphides passes off finally as sulphurous acid. Sulphides of the alkalies and of the alkaline earths, if present, are oxidized to sulphates.

Charge and fusion. 2 to 4 grammes of the sampled ore are mixed with half the assay lead required, placed in a scorifier,* and covered with the remainder of the assay lead. If borax is used, it is best placed on top of the assay, but glass should be mixed with it. The charged scorifier is placed, with help of suitable tongs, in a red hot muffle. (If no muffle is at hand, the fusion may be made in a large Hessian crucible, which is laid on its side on a good bed of coals, and partly covered with charcoal. The mouth can be closed with a crucible cover.) A piece of glowing charcoal is placed on or by the scorifier, the mouth of the muffle is closed, and the heat kept up. The lead soon fuses, and the ore, being lighter, floats on the surface and roasts. From the appearance of the fumes the assayer can frequently judge of the nature of the ore; sulphur giving light gray, zinc thick white, arsenic grayish, and antimony bluish fumes. After 15 to 20 minutes the assay has melted down, and a fluid slag has formed at the periphery of the glowing metal; the latter meantime gives off fumes of oxide of lead. With difficultly fusible ores it may require 30 minutes for complete fusion, and even then it may be necessary to add more lead or borax. The latter should be wrapped in stiff paper and placed on the assay with tongs. The paper keeps the borax from contact with the assay till its water is driven off, thus preventing a loss by sputtering. If the ore contains much zinc, it is better to volatilize this metal by covering the scorifier with glowing coals, closing the muffle and increasing the heat, as oxide of zinc forms a stiff slag. The muffle is now opened, and the slagging is allowed to proceed at a temperature just high enough to keep the lead bright. A high heat hastens the process, but causes a loss of silver by oxidation and volatilization. When the slag covers the button, the heat is increased for a few minutes, in order to separate any metallic lead which may be mechanically mixed with it. The assay is now poured into a casting-plate,† previously warmed, to expel the moisture. If no casting-plate is at hand, the assay may be allowed to cool in the scorifier.

The button should separate easily from the slag, and must be perfectly malleable. It is entirely freed from adhering slag by hammering into a cubical mass, and is then ready for the process of cupellation, unless too large, in which case it must be reduced in bulk by reheating on a fresh scorifier. If the button be hard, or contain much metallic copper, more lead and borax are added, and the process is repeated. In general it is better to carry the scorification as far as possible, since experience has shown that there is less loss of silver in scorification than in cupellation.

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* A cup of baked clay, to be had of dealers in apparatus.

† The casting-plate is a plate of sheet-copper with a handle, and 12—20 cup-shaped depressions, each 1½ inch wide and ½ inch deep; it is convenient when several assays are carried on together. The cups are rubbed with chalk to prevent the button from adhering.

3. *Cupellation* (§ 163, 10; **122**). This process consists in the oxidation of the lead on a bone-ash cupel,* which absorbs the oxide of lead, leaving metallic silver.

The cupel, after the dust is blown out, is placed in a muffle and heated to redness to expel the moisture. If this precaution be neglected, the escaping vapor causes a loss of the alloy by sputtering. The argentiferous lead is carefully placed on the cupel, a piece of glowing charcoal is laid near it, the mouth of the muffle is closed, and the whole is brought promptly to fusion. If it is not quickly fused, particles of the assay are liable to stick to the sides of the cupel, causing a loss. As soon as the assay has "cleared,"† the muffle should be opened, the charcoal removed, and the heat lowered near the assay, either by closing the draughts or moving the cupel nearer the mouth of the muffle. The oxidation should now be carried on at as low a heat as possible, as a high heat increases the volatilization of the silver along with the lead. If the temperature is right, imperfect crystals of oxide of lead form, and the fumes rise to the middle of the muffle; but if the fumes disappear immediately above the cupel, whilst the latter is at a bright red heat, and no crystals form, the heat is too high. If, on the other hand, the cupel is dark brown, and thick fumes rise to the top of the muffle, the heat is too low, and there is danger of solidification. If the assay "freezes" or solidifies, it may be again fused; the results are, however, too low, as silver passes into the bone-ash. Alloys containing copper require a higher heat to prevent freezing. Towards the close of the operation the heat should be gradually raised, as the alloy becomes less fusible with the increased proportion of silver, and the lead oxidizes with more difficulty. When the cupellation is nearly finished, a play of colors is seen, and the button suddenly brightens or "blicks," and becomes white, and is free from lead. It is immediately moved towards the mouth of the muffle, so as to cool slowly. If suddenly cooled it "sprouts," sometimes throwing particles out of the cupel, owing to the sudden escape of the oxygen which molten silver absorbs, unless it contains copper, lead, or much gold.

The button must separate easily from the cupel. It is taken up by pincers and brushed with a stiff brush. It should be well rounded and bright, show no particles of bone-ash under a magnifying glass, and have no projecting ridges caused by cracks or depressions in the cupel, as these always contain lead. The silver obtained is not chemically pure, but the amount of foreign matters is so small that no notice is taken of them in ore assays, and moreover, the impurities do not compensate for the loss in scorification and cupellation. The assay lead must be assayed, and the amount of silver yielded by it must be deducted from that obtained from the ore. The weight of silver in milligrammes, multiplied by $\frac{8.75}{3}$, gives the number of troy ounces per ton of ore.

1 Troy ounce of pure silver is worth $1.29 gold.

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* Cupels are most conveniently purchased of the dealers in apparatus. They should be neither too porous nor too compact. In the former case silver passes into the bone-ash, in the latter the oxide of lead is not absorbed with sufficient rapidity.

† *i. e.*, Exposes a bright surface of lead.

Silver ores may be assayed by the methods described in § 227 for the assay of gold ores, but the results obtained are not as high as by the scorification method.

B. ORES RICH IN SILVER.

Ores of 1 per cent. or more are assayed as described under A, but the loss by volatilization impairs somewhat the accuracy of the result.

C. BULLION.

Alloys are assayed either in the wet way or by cupellation, as described under A, 3. When the assay contains more than 1 per cent. of silver, the loss by volatilization must be taken into the account. This is done by the method of assaying with "proofs," *i. e.*, the composition of the alloy is determined approximately, if not already known, by a preliminary cupellation, and then a "proof" is made up of the same composition as the assay, by weighing off the proper quantities of pure metals; this and the assay are then melted with the same amount of lead, and the two are cupelled together side by side. The loss of the proof is added to the result of the assay. The numerous details of the assay with proofs, which are observed in order to accomplish a large amount of work in a short time, are properly learned in assay offices.

15. GOLD ASSAY.

§ 227.

Crucible Assay and Parting.

Ores of gold may also be assayed by the scorification method (§ 226), but on account of the difficulty of sampling, it is better to take larger amounts of ore and make a crucible fusion.

Gold ores may, for convenience, be divided into two classes. First, those containing little or no sulphur; and second, those containing sulphur, as pyrites, blende, etc.

A. ORES OF THE FIRST CLASS.

1. *Reduction.* If the ore consists principally of quartz or silicates, a fusion with litharge and a reducing flux yields a uniform brittle vitreous slag, and a lead button containing the gold and silver. If the ore contains basic substances, such as calcite, oxide of iron, etc., quartz sand or broken glass must be added.

The *reducing flux* mentioned in the subsequent directions is a mixture of 100 parts of bicarbonate of soda and 20 parts of flour.

The following is a convenient charge, yielding a button that may be directly cupelled:—

Ore	50 grm.
Litharge	75 grm.
Reducing flux	4 grm.

If glass is added, count it as ore, and increase the litharge and reducing flux proportionally.

Mix thoroughly; place the mixture in a clay crucible, which should not be more than two-thirds filled. Cover one-quarter inch deep with dry chloride of sodium, and lute on the cover, or the luting may be omitted if care be taken that no coals get into the crucible. The fusion may be made in any furnace in which a white heat is obtainable, best in a deep wind furnace.

The fire is kindled at the top, so that the heat shall be gradually raised to prevent the crucible cracking. A dull red heat is kept up for half an hour, and a white heat for a quarter of an hour longer. Too high a heat for an unnecessary length of time is to be avoided, as the litharge is liable to flux the crucible. Remove from the fire while hot, and tap gently on the hearth to collect the lead into a button. When cool, crack out the button, which should separate readily from the slag, and be perfectly malleable. The slag should be uniform and vitreous, showing a perfect fusion, and should include no metallic globules.

2. *Cupellation.* The button contains the gold and silver, and is cupelled as directed, p. 530. A higher heat is, however, necessary to remove the last traces of lead than if no gold were present. There is no danger of sprouting if the alloy contains much gold.

3. *Parting.* Clean the gold globule, as directed p. 530, weigh, and add pure silver if necessary, so that the alloy shall contain 2½ parts silver to 1 of gold. The proportion of additional silver required in an ore-assay may be commonly judged from the color of the alloy. If it is bright yellow, add 2½ parts, if only faint yellow, 2 parts, and if white, 1 part or less.

The silver and the alloy are fused together on charcoal before the blowpipe, or, better still, are wrapped in sheet lead, and cupelled at a high heat. The button is hammered and rolled into a long thin leaf, care being taken that no particles crack off. If large, it must be annealed during the rolling, by heating on a cupel in the muffle.

The leaf is rolled together on a slender rod or pencil, and placed in an assay flask, or large test-tube, and boiled with dilute nitric acid, sp. gr. 1·16, till all action has ceased; the acid is decanted, and the boiling repeated with acid of sp. gr. 1·30.

Wash the residual gold with water free from chlorine till the washings give no reaction for silver, fill the flask with water, cover its mouth with a drying-cup * or porcelain crucible, and invert. The gold quickly settles to the bottom of the cup. The flask is slowly raised till the cup is nearly full of water, and is then quickly drawn off one side. The water is carefully poured out of the cup, and the gold, if in separate particles, is collected in a drop of water at the bottom. After thoroughly drying, heat to redness in the muffle, but not to fusion. If the process has been properly conducted the gold remains in one coherent mass, and may be readily turned into a weighing-cup. The litharge must be assayed for silver with the same reducing flux as was used with the ore.

The weight of the button obtained by cupellation, less that of the silver yielded by the litharge, less that of the gold, is the weight of the silver in the ore.

The ounces per ton are calculated as directed p. 530, bottom.

1 Troy ounce of gold has a value of $20.66.

B. Ores of the Second Class (containing Sulphur).

1. *Roasting Process.* The object of roasting is to expel the sulphur, but this process is objectionable on account of the mechanical loss of gold occasioned by it. The operation is conducted as follows: A weighed

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* The drying-cup is a deep narrow vessel of biscuit ware.

amount of the ore is placed in an iron pan, the bottom and sides of which have been smeared with a paste of clay, or Venetian red, and water. This coating serves to protect the iron from the action of sulphur, and should be slowly and thoroughly dried to prevent cracking. The roasting is carried on at a dull red heat, with frequent stirring, until most of the sulphur is driven off. Towards the close of the process the heat is raised, and is kept up till the odor of sulphurous acid is no longer perceptible, and a moistened blue litmus paper held a few inches above the ore remains unchanged. The ore and scrapings from the pan are pulverized and sifted. The following are the proportions of the charge:

50	grms. of ore.	
20	"	powdered glass.
15	"	reducing flux.
100	"	litharge.

Fuse in a crucible and cupel, as directed for ores of the first class.

2. *Assay by Litharge and Nitre.* In crucible fusions of auriferous sulphides, advantage is taken of their reactions with oxide of lead. If sulphides are fused with sufficient litharge, a button of lead and a slag free from sulphur, or containing the sulphates of the alkalies or alkaline earths, are obtained, but the lead button is too large for scorification. Pyrite reduces 8½ parts, chalcopyrite and blende 7 parts, gray copper and sulphide of antimony about 6 parts of lead. Nitre is added to prevent too much lead being reduced; and, to determine the amount of nitre proper to use, a preliminary assay is made by fusing 3 to 5 grm. of the ore with 50 parts of litharge. The fusion should be made quickly, using care to prevent the action of reducing gases, and as soon as the mass ceases to boil, the crucible should be removed from the fire, to prevent the litharge destroying it. The resulting button is weighed, and the amount of lead that would be yielded by the ore required for an assay is calculated. If this amount would be too small for cupellation, reducing flux must be added; if of the right size, neither reducing flux nor nitre is necessary, but, if too large, nitre must be added. To find the weight of nitre required in the last case, deduct the weight of the button desired for cupellation (10—15 grm.) from the weight of the lead which would be produced by fusing the charge of ore with litharge alone, and divide the remainder by four; the result is the weight of nitre required. The oxidizing power of commercial nitre varies so much that it is better to determine it by fusing a sample with litharge and a reducing flux. The weight of lead which the flux alone produces, less that obtained when a given weight of nitre is added, is the weight of lead oxidized by the nitre. The charge is made of the following proportions:

Ore, 20 grm.
Litharge, 100 to 160 grm., according to the proportion of the sulphides.
Nitre, amount calculated.
Bicarb. soda, 20 grm.

Mix thoroughly, place in a thick French crucible, which should not be more than one-third filled, and put on top 20 grm. of borax, and a covering of common salt. The fusion is made slowly, to prevent the assay from running over, and is kept at a strong heat for an hour. The button should be malleable, and the slag should give no odor of sulphuretted hydrogen when treated with sulphuric acid. It is cupelled as directed, p. 530 (if too large it is first scorified), and the gold and silver parted as directed p. 532.]

16. ASSAY OF ZINC ORES.

§ 228.

Method of SCHAFFNER,* *modified by* C. KÜNZEL,† *as employed in the Belgian zinc-works ; described by* C. GROLL.‡

a. Solution of the ore and preparation of the ammoniacal solution.

Powder and dry the ore.

Take 0·5 grm. in the case of rich ores, 1 grm. in the case of poor ores, transfer to a small flask, dissolve in hydrochloric acid with addition of some nitric acid by the aid of heat, expel the excess of acid by evaporation, add some water, and then excess of ammonia. Filter into a beaker, and wash the residue with lukewarm water and ammonia, till sulphide of ammonium ceases to produce a white turbidity in the washings. The oxide of zinc remaining in the hydrated sesquioxide of iron is disregarded. Its quantity, according to GROLL, does not exceed 0·3—0·5 per cent. This statement probably has reference only to ores containing relatively little iron; where much iron is present the quantity of zinc left behind in the precipitate may be not inconsiderable. The error thus arising may be greatly diminished by dissolving the slightly washed iron precipitate in hydrochloric acid and adding excess of ammonia. But the surer mode of proceeding is to add to the original solution—after evaporating off the greater part of the free acid as above, and allowing to cool—dilute carbonate of soda nearly to neutralization, then to precipitate the sesquioxide of iron, after p. 202, *d*, with acetate of soda, boiling, to filter, and wash. The washings, after being concentrated by evaporation, are added to the filtrate and the whole is then mixed with ammonia, till the first-formed precipitate is redissolved.

If the ore contains manganese—provided approximate results will suffice—digest the solution of the ore in acids, after the addition of excess of ammonia and water, at a gentle heat for a long time, and then filter off, with the iron precipitate, the hydrated protosesquioxide of manganese which has separated from the action of the air. The safer course—though undoubtedly less simple—is, after separating the iron with acetate of soda, to precipitate the manganese by passing chlorine, as directed p. 357, **59**, or by adding bromine and heating.

If lead is present, it is separated by evaporating the aqua regia solution with sulphuric acid, taking up the residue with water and filtering; then proceed as directed.

b. Preparation and standardizing of the sulphide of sodium solution.

The solution of sulphide of sodium is prepared either by dissolving crystallized sulphide of sodium in water (about 100 grm. to 1000—1200 water), or by supersaturating a solution of soda, free from carbonic acid, with sulphuretted hydrogen, and subsequently heating the solution in a flask to expel the excess of sulphuretted hydrogen. Whichever way it is prepared, the solution is afterwards diluted, so that 1 c. c. may precipitate about 0·01 grm. zinc. Prepare a solution of zinc, by dissolving 10 grm. chemically pure zinc in hydrochloric acid, or 44·122 grm. dry crystallized sulphate of zinc in water, or 68·133 grm. dry crystallized sulphate of potash and zinc in water, and making the solution in either case up to 1 litre with water.

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* Journ. f. prakt. Chem. 73, 410.

† Ibid. 88, 486.

‡ Zeitschrift f. anal. Chem. 1, 21.

Each c. c. of this solution corresponds to 0·01 grm. zinc. Now measure off 30—50 c. c. of this zinc solution into a beaker, add ammonia till the precipitate is redissolved, and then 400—500 c. c. distilled water. Run in sulphide of sodium as long as a distinct precipitate continues to be formed, then stir briskly, remove a drop of the fluid on the end of a rod to a porcelain plate, spread it out so that it may cover a somewhat large surface, and place in the middle a drop of pure dilute solution of chloride of nickel. If the edge of the drop of nickel solution remains blue or green, proceed with the addition of sulphide of sodium, testing from time to time, till at last a blackish gray coloration appears surrounding the nickel solution. The reaction is now completed, the whole of the zinc is precipitated, and a slight excess of sulphide of sodium has been added. The precise depth of color of the nickel must be observed and remembered, as it will have to serve as the stopping signal in future experiments. To make sure that the zinc is really quite precipitated, you may add a few tenths of a c. c. more of the reagent, and test again, of course the color of the nickel-drop must be darker. Note the number of c. c. used, and repeat the experiment, running in at once the necessary quantity of the reagent, *less* 1 c. c., and then adding 0·2 c. c. at a time, till the end-reaction is reached. The last experiment is considered the more correct one. The sulphide of sodium solution must be restandardized before each new series of analyses.

c. Determination of the zinc in the solution of the ore.

Proceed in the same way with the ammoniacal solution prepared in *a* as with the known zinc solution in *b*. Here also repeat the experiment, the second time running in at once the required number of c. c., less 1, of sulphide of sodium, and then adding 0·2 c. c. at a time, till the end-reaction makes its appearance. The second result is considered the true one. There are three different ways in which this repetition of the experiment may be made. You may either weigh out at the first two portions of the zinc ore, or you may weigh out double the quantity required for one experiment, make the ammoniacal solution up to 1 litre and employ ½ litre for each experiment, or lastly, having reached the end-reaction in the first experiment, you may add 1 c. c. of the known zinc solution, which will destroy the excess of sulphide of sodium, and then run in sulphide of sodium in portions of 0·2 c. c., till the end-reaction is again attained. Of course, in this last process to obtain the second result, you deduct from the whole quantity of sulphide of sodium used the amount of the same, corresponding to 1 c. c. of the zinc solution.

If the ore contains copper, remove it from the acid solution by sulphuretted hydrogen, evaporate the filtrate with nitric acid, dilute, treat with ammonia, and determine the zinc as above.

17. ANALYSIS OF CAST IRON, STEEL, AND WROUGHT IRON.

§ 229.

Cast iron, one of the most important products of metallurgic industry, contains a whole series of elements, mixed in greater or less proportion with the iron, or combined with it. Although the influence which the various foreign substances mixed with the iron exercise on the quality of cast iron is not yet accurately known, still the fact that they do exercise considerable influence on the quality of the article is beyond doubt. The analysis of cast iron is one of the more difficult problems of analytical chemistry. The following bodies must be had regard to in the analysis:—

Iron, *carbon* combined with the iron, carbon in form of *graphite*, nitrogen, *silicon*, *phosphorus*, *sulphur*, potassium, sodium, lithium, calcium, magnesium, aluminium, chromium, titanium, zinc, *manganese*, cobalt, nickel, *copper*, tin, arsenic, antimony, vanadium. As a general rule, the elements in italics alone are quantitatively determined.

Steel and wrought iron are analyzed in the same manner as cast iron.

1. *Determination of the Carbon.*

a. Determination of the total amount of Carbon.

Method of BERZELIUS (somewhat modified.)

Treat about 3 grm. of the cast iron, or 5—10 grm. of steel, moderately comminuted,* with a neutral concentrated solution of chloride of copper, (made by mixing hot solutions of chloride of sodium and sulphate of copper, and allowing sulphate of soda to crystallize out), and let the mixture stand at the common temperature † with occasional stirring. In 5 or 6 hours, or as soon as the part remaining undissolved presents a mixed mass of copper and separated carbon, &c., crumbling under pressure, add hydrochloric acid, and, if necessary, some more chloride of copper, and digest until the whole of the copper is dissolved to subchloride. At this stage of the process a gentle heat may be applied. Filter through a tube of the form shown in fig. 100, the narrow part of which is loosely stopped with spongy platinum or asbestos, ignited in a current of moist air. Wash well, dry thoroughly, and treat the entire contents of the tube either as directed § 176 or § 178. After emptying

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[* Best by drilling, in case of gray pig or soft steel. White pig is reduced to powder by aid of the steel mortar.]

† On warming, a small quantity of gas is evolved, which contains a trifling admixture of carbonetted hydrogen. [Sometimes gas escapes at ordinary temperatures. In that case a lump of ice should be placed in the vessel at first. After an hour or so cooling is unnecessary.]

the tube, rinse with a little chromate of lead or oxide of copper; if the combustion is to be effected in a boat, in a current of oxygen gas, in order that the incombustible residue may be examined, rinse with oxide of mercury.

b. Determination of the Graphite.

Treat another portion of the cast iron with moderately concentrated hydrochloric acid, at a gentle heat, until no more gas is evolved; filter the solution through asbestos that has been ignited in a stream of moist air or through spongy platinum (comp. *a*,), wash the undissolved residue, first with boiling water, then with solution of potassa, after this with alcohol, and lastly with ether (MAX BUCHNER);* then dry, and burn after § 176 or § 178. Direct weighing is not advisable, as the graphite generally contains silicon. Deduct the graphite obtained here from the total amount of carbon found in *a*; the difference gives the combined carbon.

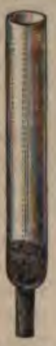

FIG. 100.

2. *Determination of the Sulphur.*

The safest way of estimating sulphur in cast iron is the following:—Put about 10 grm. of the substance, in the finest possible state of division, into the flask *a* (fig. 101), insert the cork,† containing the funnel-tube *d c*, and the evolution tube *f*; the funnel-tube is provided with a little mercury at *i*, and the evolution tube is connected with two U-tubes, which contain a strongly alkaline solution of lead. Fill the funnel *d* with hydrochloric acid, and suck by means of an India-rubber tube at the exit of the second U-tube, in which a small glass tube is inserted; the acid will thus pass into the flask. Heat the flask, sucking in more acid from time to time as just described, till complete solution of the iron is effected; then connect the exit of the second U-tube with an aspirator, and draw air through the apparatus for a long time. Collect the sulphide of lead on a small filter, fuse it cautiously with a little nitre and carbonate of soda, soak in water, pass carbonic acid, to precipitate traces of dissolved lead, filter, acidify the filtrate with hydrochloric acid and precipitate the sulphuric acid with chloride of barium.

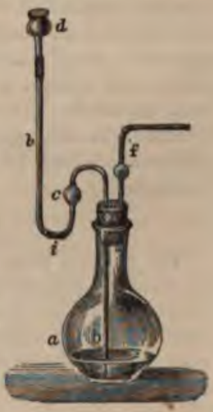

FIG. 101.

To make quite sure that you have left no sulphur behind, before throwing away the contents of the flask, evaporate the solution of protochloride of iron, to drive off excess of hydrochloric acid, and test it with chloride of barium; also fuse the undissolved residue with nitre and carbonate of soda, and test the aqueous extract of the fused mass for sulphuric acid. As a rule the residue will be found free from sulphur. But if any sulphate of baryta is obtained again here, it may be collected on the same filter which has received that produced from the sulphide of lead.

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* Journ. f. prakt. Chem. 72, 364.

† If a caoutchouc stopper were used, a little sulphur would not be unlikely to get into the residue; the caoutchouc connections must be desulphurized.

[3. *Estimation of Phosphorus.*

In case of cast iron, when the amount of phosphorus present exceeds 1 per cent., 2 grm. suffice for a determination; when less is present it is best to take at least 3 grm. Treat with aqua regia in a tall beaker covered with a watch-glass. Digest at a moderate temperature 2 or 3 hours, or till effervescence ceases, then remove the cover and evaporate to dryness, as in the ordinary way of separating silica, with addition of nitric acid, if need be, to remove chlorine. A temperature a few degrees above that attainable with the water-bath may be used to hasten this operation. But if too high heat is used, oxide of iron will remain undissolved on subsequent treatment with nitric acid; moreover, pyrophosphate may be formed at a temperature below 150° C. After the residue has been dried sufficiently to make the silica insoluble, digest with nitric acid till the iron is dissolved. Separate the residue by filtering, and reserve it for determination of silicon. To the filtrate add 100 c. c. of molybdic acid solution. If after the addition of this reagent the solution amounts to less than 350 to 400 c. c., dilute to that volume.

Place for 24 hours in a warm situation where the temperature does not rise above 40° C. Wash the precipitate with the molybdic solution, diluted with an equal volume of water, letting the washings run into the filtrate. Then allow the filtrate to stand 24 hours or more in a warm place, and collect any appreciable amount of phospho-molybdate that may separate. Dissolve and reprecipitate according to p. 271.

Steel (3—10) grm. may be dissolved in nitric acid of 1·20 sp. gr., and evaporation to dryness may be omitted when silicon is not to be estimated.]

[4. *Estimation of Silicon.*

The residue from the solution used for determining phosphorus may be used for determining silicon. Ignite it without separation from the filter until the graphite is partially burned away. Fuse with carbonate of soda mixed with a little nitrate of potash, sufficient to effect complete combustion of the carbon still present. Treat the fused mass first with boiling water, in which it readily dissolves, except some silica in light flocculent form, and traces of metallic oxides. Acidify with hydrochloric acid, or nitric acid, in case the solution is to be in contact with platinum, and separate silica as usual. When the quantity of silica is not over 1 per cent., these operations may be most conveniently performed in a large platinum crucible without transferring the substance to any other vessel.]

[5. *Estimation of Manganese and Cobalt.*

2 grm. is as large a quantity as can conveniently be treated by the method here proposed, and will in most cases suffice. Where less than 2 per cent. is present, and great accuracy is required, it is necessary perhaps to take more. Of *spiegeleisen* 1 to ½ grm. suffices. Prepare a

solution of the iron in the same manner as for phosphorus (3). A higher temperature may, however, be used to make silica insoluble, and hydrochloric acid may be used for redissolving. Filter from the residue of carbon and silica into a large flask. When the solution is cold, add carbonate of soda as long as the precipitate formed by it can be redissolved by shaking and letting stand a few minutes. Next add 12 to 15 c. c. strong acetic acid, and the same volume of a saturated solution of acetate of soda. Dilute, now, the solution to about 1 litre, and precipitate iron by boiling. Filter and wash without decantation, as long as the water passes freely through the mass upon the filter. When the washing becomes tedious, on account of slow passage of water through the filter, rinse the precipitate from the filter into a dish with a jet of water, and boil with a moderate amount of water with addition of a little acetate of soda, stirring with a glass rod as long as any coherent lumps of precipitate remain. Bring the precipitate back again upon the filter and complete the washing. Concentrate the filtrate and washings to about 300 c. c. (or less if too much saline matter is not present). A little iron is usually present in this filtrate; sometimes it is partially deposited during the evaporation. In order to separate the manganese from this, and from the large quantity of saline matter in the liquid, precipitate next all the metallic oxides present by gradually adding carbonate of soda to the boiling solution as long as a precipitate is formed, and adding at the close a few drops of caustic soda. Filter, wash the precipitate slightly, dissolve it on the filter with hydrochloric acid, and separate the small quantity of iron in the new solution with acetate of soda. For this purpose, when, as usually is the case, but little iron is present, the solution need occupy but a small volume (100 c. c.). Add carbonate of soda as long as no permanent precipitate is formed, then 2 or 3 c. c. of the acetate of soda solution, and heat gradually to boiling. Sometimes when this solution is moderately warmed, and carbonic acid has mostly escaped, but before the temperature is high enough to precipitate the iron, the solution will become turbid with a finely divided white precipitate. If this happens, add acetic acid till it dissolves, and then raise the heat to boiling. Filter from the precipitated iron, and precipitate *manganese* in the filtrate with bromine (see § 223,2). When no great accuracy is required, this precipitate may be washed, ignited, and weighed as protosesquioxide of manganese, and metallic manganese calculated from it. It may, however, contain cobalt, which is often present in pig iron, and possibly traces of copper.

To detect the presence of *cobalt*, dissolve the weighed oxide of manganese in a few drops of HCl, heat till the brown color imparted by the manganese disappears. A comparatively small amount of cobalt will now give the solution, while hot and concentrated, a bright green color that disappears on diluting with cold water. Evaporate the solution till free acid is expelled, dissolve in a small quantity of water, add acetate of soda and a drop of acetic acid, heat to boiling and transmit HS, which will precipitate the cobalt. Collect the precipitate on a filter, wash rapidly with water containing HS. Testing this precipitate with a blowpipe will further confirm its nature. If it be judged from this examination that cobalt is present in any sensible quantity, evaporate the filtrate last obtained till HS is expelled, and precipitate manganese again with carbonate of soda, and weigh it as protosesquioxide.

For most practical purposes sufficiently good results may be usually obtained in the analysis of *spiegeleisen*, e. g., by separating iron from a solution of 0·5—0·7 grm. as above described, precipitating the concentrated filtrate directly by means of phosphate of soda and weighing the manganese as pyrophosphate. See p. 185.]

5. *Determination in one portion of the total amounts of silicon, iron, manganese, zinc, cobalt, nickel, alumina, titanic acid, alkaline earths and alkalies.*

Dissolve about 10 grm. of the cast iron in a capacious platinum dish,* in moderately dilute hydrochloric acid, evaporate with a few drops of dilute sulphuric acid on the water-bath to dryness, till the mass ceases to smell of hydrochloric acid, moisten with hydrochloric acid, heat, add water, filter, wash and dry the precipitate. Let us call it *a*. Heat the solution in a porcelain dish with nitric acid, dilute copiously and precipitate the sesquioxide of iron, &c., by nearly saturating with carbonate of ammonia and boiling, after p. 362, **69.** Wash and dry the precipitate; call it *b*.

Mix the filtrate from *b* with ammonia in slight excess, heat till the excess of ammonia is almost expelled, filter, dissolve in hydrochloric acid and reprecipitate in the same manner. Filter, wash and dry the precipitate; call it *c*.

Acidify the filtrate from *c* with hydrochloric acid, concentrate in a porcelain dish, transfer to a flask, add ammonia and sulphide of ammonium and proceed generally as directed p. 184, *c*. After 24 hours, filter the precipitate (*d*) off, wash it with water containing sulphide of ammonium, spread the filter on a glass plate, rinse the precipitate into a flask, treat it with acetic acid, cork and set aside.

Evaporate the filtrate from *d* in a platinum dish to dryness, expel the ammonia salts at the lowest temperature possible, and in the residue determine the alkaline earths and alkalies. For this purpose precipitate the lime by pure oxalate of ammonia repeating the precipitation according to **29,** and from the filtrate separate magnesia according to **16.** The alkalies are weighed as chlorides and potassa is finally estimated by **1.**

The residue *a* contains the whole of the bodies insoluble or difficultly soluble in hydrochloric acid. The following substances may be present besides carbon and silica, viz., phosphide of iron, chromium-iron, vanadium-iron, arsenide of iron, carbide of iron, silicon, molybdenum, &c., and also slag in a more or less altered condition. Titanic acid and sulphate of baryta may also be here present. Fuse with carbonate of soda and potash, and a little nitre, separate the silica as usual, by evaporating with hydrochloric acid and two drops of dilute sulphuric acid, weigh it and see whether it is pure (comp. p. 300); the impurities most likely to be present are sulphate of baryta and titanic acid. The silicic acid may have been partially formed from silicon, and partially present as such in the slag. In the filtrate from the silicic acid separate what is separable by ammonia by double precipitation, filter off the precipitate (*c′*), then precipitate with sulphide of ammonium, filter off the precipitate (*d′*, to be treated as *d*) and finally test the filtrate for alkaline earths, any small quantities of which found can then be weighed with the somewhat larger amount obtained above.

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* If glass or porcelain be used, the estimations of the silicon and aluminium cannot be considered as absolutely exact.

The precipitates *b*, *c* and *c'* contain the whole of the sesquioxide of iron and alumina, also that part of the titanic acid which has passed into solution. Transfer the mixed ignited precipitates to several platinum or porcelain boats, put these in a glass tube and ignite in pure hydrogen, till no more steam issues. Treat the boats and their contents with very dilute nitric acid (1 of acid to 30—40 of water) to dissolve the iron, make the solution up to 1000 c. c. and determine the iron in an aliquot part by oxidation and precipitation with ammonia.* Fuse the residue, which was insoluble in the very dilute nitric acid, with bisulphate of potash, take up with cold water, filter off any residual silica, collect and weigh it and add the weight to that found above; pass sulphuretted hydrogen, endeavor to precipitate any titanic acid that may be present by boiling and passing a stream of carbonic acid, boil the filtrate or the clear solution with nitric acid, precipitate the alumina with ammonia, and separate it from the small quantity of sesquioxide of iron that may possibly be present by the method given p. 521 (precipitate. II). In this, as in that case, regard must be paid to phosphoric acid, as its presence would give fictitious weight to the alumina. If chromium were present, its oxide would likewise have to be separated and determined in this precipitate.

The precipitates *d* and *d'* have given up to the acetic acid almost the whole of their sulphide of manganese. Filter off the solution, suspend the residue in sulphuretted hydrogen water, and add some hydrochloric acid. Under these circumstances, the sulphide of zinc and any residual sulphide of manganese are dissolved, while the sulphide of copper (which is not here estimated), sulphide of nickel, and sulphide of cobalt are left behind. Evaporate the hydrochloric acid solution to a small bulk, boil with excess of solution of soda, precipitate any zinc from the solution by sulphuretted hydrogen, dissolve any separated hydrate of protosesquioxide of manganese in hydrochloric acid, add the solution to the acetic acid solution, and determine the manganese in the mixture. Incinerate the filter, containing the sulphides of copper, nickel and cobalt, dissolve in hydrochloric acid, precipitate with sulphuretted hydrogen, and in the filtrate thus freed from copper estimate the nickel and cobalt.

6. *Determination in one portion of the metals of Groups* V. and VI. *and of the phosphorus.*

Treat 10 grm. of the cast iron in the finest possible state of division with a previously heated mixture of 1 volume of nitric acid and 3 volumes of hydrochloric acid (both acids must be pure and strong) in a very capacious, long-necked, obliquely placed flask at a gentle heat. When all visible action has ceased, decant the solution and treat the residue with a fresh portion of aqua regia.† Mix the solutions, dilute copiously and treat in a large flask with sulphuretted hydrogen, at first in the cold, then at 70°. I may here observe that the solution usually retains a brownish tint from dissolved organic substances, even after the sesquichloride of iron is reduced. Allow the fluid (saturated with sulphuretted hydrogen) to settle for 24 hours, filter, dry the precipitate, which consists principally of sulphur, and extract it with warm bisulphide of carbon. There usually remains a small black residue, which often contains, besides sulphide of copper, a little sulphide of arsenic and sulphide of antimony. Separate these, or generally the metals present of the fifth and sixth groups, according to the methods given in Section V.

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* It is not advisable to determine the iron in a separately weighed smaller quantity, unless the sample to be examined is perfectly homogeneous.

† Instead of aqua regia, bromine and water may be used. The solution goes on rapidly, at first almost violently, if the bromine is in excess and the mixture is digested at 20°—30°. Toward the end assist the action by the heat of a water-bath (J. Nicklès). If this method is employed, I should still recommend that the residue be treated with aqua regia.

Free the filtrate from the sulphuretted hydrogen precipitate from the excess of the gas by transmission of carbonic acid, add a little pure sesquichloride of iron, nearly neutralize the solution with pure carbonate of soda and precipitate with carbonate of baryta in a closed flask. Treat the precipitate, which contains the whole of the phosphoric acid (produced by the oxidation of the phosphorus compounds), with hydrochloric acid, precipitate the baryta with sulphuric acid, filter, evaporate to small bulk, precipitate the phosphoric acid with solution of molybdenum and determine it after p. 271, β.

As a portion of the phosphide of iron may have escaped oxidation by the aqua regia, fuse the residue insoluble therein with carbonate of soda and nitre, and test the aqueous solution of the fused mass likewise for phosphoric acid.

18. ANALYSIS OF MANURES.

§ 231.

I SPEAK here simply of the manures which owe their origin to the urine, excrements, blood, bones, &c., of animals, or are prepared by the decomposition of apatite, &c., by acids. The examination of manures has chiefly a practical object, and demands accordingly simple methods. The value of a manure depends upon the nature and condition of its constituents. The following constituents are the most important:—organic matters (characterized by their carbon and nitrogen), ammonia salts, nitrates, phosphates, sulphates, and chlorides with alkaline and alkaline earthy bases (potassa, soda, lime, magnesia). To these substances we know the efficacy of a manure is owing, but as to the condition in which they exercise the most favorable action, our views are much less clear; indeed, it is obvious that a universally applicable and valid rule cannot well be laid down in this respect; since the agriculturist sometimes wishes a manure containing most of its constituents in a state of solution, which will accordingly exercise a speedy fertilizing action, and sometimes one which will only gradually supply the soil with the substances required by the plants. As regards the insoluble materials of manures, it may be safely asserted that their value advances in proportion as their degree of division and solubility increases.

I will here give, 1, the outlines of a general method of examination applicable to almost all kinds of manures; 2, methods of valuing guano and manures prepared from bones, apatite, &c.

A. General Process.

§ 232.

Mix the manure uniformly by chopping and grinding, then weigh off successively the several portions required for the various estimations.

1. *Determination of the Water.*—Dry 10 grm. at 125°, and determine the loss of weight (§ 29). (It is rarely necessary to make a correction on account of the carbonate of ammonia which escapes with the water.*)

2. *Total Amount of fixed Constituents.*—Incinerate, at a gentle heat, a weighed portion of the residue left in 1, in a thin porcelain dish; moisten the ash with a solution of carbonate of ammonia, dry, ignite gently, and weigh.

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* To do so, dry the manure in a boat inserted in a tube; the tube is heated to 100° in the water- or air-bath, a current of air being transmitted through it, by means of an aspirator: the air enters through concentrated sulphuric acid, and makes its exit through two U-tubes containing standard sulphuric acid. After drying, the quantity of ammonia expelled, which has combined with the standard acid, is determined (§ 99, 3).

3. *Constituents soluble in Water, and insoluble in Water.*—Digest 10 grm. of the fresh manure with about 300 c. c. water, collect the residue on a weighed filter, wash, dry at 125°, and weigh. The weight found expresses the total quantity of the substances insoluble in water, and the difference—after deducting the water found in 1—gives the amount of the soluble constituents. Incinerate now the insoluble residue, treat with carbonate of ammonia, as in 2, and weigh; the weight expresses the total amount of the fixed constituents contained in the insoluble part, and the difference between this and the ash in 2 gives the total amount of fixed constituents contained in the soluble part.

4. *Fixed Constituents singly.*—[Obtain 3—5 grm. of ash according to 2. Treat 2 grm. with hot dilute hydrochloric acid until only *insoluble matters* (sand, clay, and charcoal) remain, which filter off, wash, ignite, and weigh. The filtrate and washings are brought to the bulk of 200 c. c., mixed, and divided into four equal parts.

a. To 50 c. c. add ammonia until a slight permanent precipitate is formed, then enough hydrochloric acid to dissolve this precipitate, heat to boiling, and add acetate of soda as long as a precipitate forms, wash, ignite, and weigh. Two cases may here present themselves.

α. If the precipitate before ignition were red it contains all the iron, alumina, and phosphoric acid. In this case dissolve it in concentrated hydrochloric acid with cautious addition of sulphuric acid, towards the last, finally evaporate off the hydrochloric acid (or fuse with carbonate of soda and dissolve in sulphuric acid) and determine the *sesquioxide of iron* volumetrically (p. 203). Afterwards in the same liquid determine *phosphoric acid* by molybdic solution (p. 271). Calculate *alumina* by difference. In the filtrate from the acetate of soda precipitate, determine *lime* as oxalate, and afterwards *magnesia* as pyrophosphate, according to **29**, p. 349.

β. If the precipitate before ignition were nearly white, it contains all the iron and alumina and a portion of the phosphoric acid. It may be analyzed as just described, or, if very small in quantity, half of it may be reckoned as phosphoric acid (see page 141). From the filtrate containing free acetic acid, *lime* is precipitated as oxalate (**30**, p. 350), the second filtrate is then neutralized by ammonia, when all the *magnesia* and a portion of *phosphoric acid* go down as ammonio-phosphate of magnesia; the third filtrate is treated with magnesia-mixture to separate the rest of the *phosphoric acid.*

b. To another 50 c. c. add hot concentrated solution of caustic baryta in slight excess, boil, and filter. The filtrate (and washings) containing only alkali chlorides and chlorides of barium and calcium, is treated hot with solution of carbonate of ammonia and some caustic ammonia, filtered from carbonates of baryta and lime, the liquid evaporated and ignited to expel ammonia-salts, and this process repeated, if need be, until pure alkali chlorides are obtained (see p. 303, last paragraph), in which the *potassa* and *soda* are determined according to **1**, p. 339, or **5**, p. 342.

c. In a third portion of 50 c. c., estimate *sulphuric acid* by precipitation with chloride of barium.

The fourth 50 c. c. is reserved for use in case of accidents.]

d. Determine the *carbonic acid* in another portion of the ash, as directed p. 291, *c c*, or p. 293, *e*. Filter the contents of the flask (in which the solution has been effected with the aid of dilute nitric acid), and precipitate the chlorine with solution of nitrate of silver, as directed § 141, I., *a*.

5. *Total amount of Ammonia.*—Treat a weighed portion of the manure by SCHLÖSING's method (p. 158, *b**).

6. *Total amount of Nitrogen.*—Moisten a weighed portion of the manure with a dilute solution of oxalic acid in sufficient quantity to impart a feebly acid reaction; dry, and determine the nitrogen, in the entire mass or in a weighed portion, after § 185. If you deduct from the total amount of nitrogen so found the quantity corresponding to the ammonia and the nitric acid, the difference shows the quantity of nitrogen contained in the organic substances. It is generally sufficient, however, to know the total amount of the nitrogen.

7. *Total amount of Carbon.*—Treat a portion of the dried residue of 1 by the process of organic analysis (§ 189). If the dried manure contains carbonates, determine the carbonic acid in a separate portion, and deduct the result from the total amount obtained by the organic analysis; the difference shows the quantity of carbonic acid formed in the latter process by the carbon of the organic substances.

8. *Nitric Acid.*—Treat a weighed portion of the manure with water, and evaporate the solution, with addition of pure carbonate of soda to distinct alkaline reaction; filter after some time, then evaporate the filtrate to a small bulk, and determine in fractional parts of it the nitric acid. As the solution will scarcely ever be free from organic matter, employ SCHLÖSING's method (p. 331).

B. ANALYSIS OF GUANO.

§ 233.

Guano consists of the excrements of sea-fowls, more or less altered. It not only varies very considerably in quality in the different islands from which our supplies are derived, but is often also fraudulently adulterated with earth, brick-dust, carbonate of lime, and other matters.

The guano is mixed as uniformly as possible, and that which is intended for analysis is put into a stoppered bottle.

1. *Determination of the Water.*—This is effected exactly as on p. 543 (1). In exact analyses the carbonate of ammonia must not be overlooked—(see note). Genuine guano loses from 7 to 18 per cent.

2. *Total amount of fixed Constituents.*—Incinerate a weighed portion in a porcelain or platinum crucible placed in a slanting position, and weigh the ash. Good guano leaves from 30 to 33 per cent. of ash, guano of bad quality from 60 to 80 per cent., and a wilfully adulterated article often even more. The ash of genuine guano is white or gray. A yellow or reddish color indicates adulteration with loam, sand, or earth. In the first stage of the decomposition by heat, good guano emits a strong ammoniacal odor and white fumes.

3. *Constituents soluble in Water, and insoluble in Water.*†—Heat 10

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* Small quantities of ammonia are determined with *deci*normal sulphuric acid.

† It must be mentioned that the quality and quantity of the constituents soluble in water are by no means constant for the same guano. Liebig (Annal. d. Chem. u. Pharm., 119, 13) has shown that the kind of salts which pass into solution varies according to whether one filters the solution off immediately or after

grm. guano with about 200 c. c. water, collect the residue on a weighed filter without delay, and wash it with hot water, until the water running off looks no longer yellowish and leaves no residue when evaporated upon platinum foil; dry the residue, and weigh. Deduct the sum of the water and the residue from the weight of the guano; the remainder expresses the amount of the soluble constituents. Incinerate the residue and weigh the ash; the difference shows the amount of the fixed soluble salts. With very superior sorts of guano, the residue insoluble in water amounts to from 50 to 55 per cent., with inferior sorts, to from 80 to 90 per cent. The brown-colored aqueous solution of genuine guano evolves ammonia upon evaporation, emits a urinous smell, and leaves a brown saline mass, consisting chiefly of sulphates of soda and potassa, chloride of ammonium, oxalate and phosphate of ammonia.

4. *Fixed Constituents singly.*—As in § 232.
5. *Total amount of Ammonia.* "
6. *Total amount of Nitrogen.* "
7. *Total amount of Carbon.* "
8. *Nitric Acid.* "

9. *Carbonic Acid.*—Employ one of the methods § 139, II. Genuine guano contains only a small proportion of carbonates. If, therefore, a guano effervesces strongly when moistened with dilute hydrochloric acid, this may be regarded as a proof of adulteration with carbonate of lime.

10. *Uric Acid.*—If it is wished to ascertain the quantity of uric acid which a guano contains, treat the part insoluble in water with a weak solution of soda at a gentle heat, filter, and acidify the filtrate with hydrochloric acid, to precipitate the uric acid. Collect on a weighed filter, wash cautiously with the least possible quantity of cold water, dry, and weigh.

11. *Oxalic Acid.*—As appears from the note to 3, the oxalate of ammonia in guano plays an important part with respect to the solution of the phosphate of lime. It is, therefore, frequently a matter of interest to determine the oxalic acid. This is best done in a separate portion after § 137, *d*, *β*. A little dilute sulphuric acid is first made to act upon the guano, till all the carbonic acid is expelled, the sulphuric acid is then neutralized with solution of soda free from carbonic acid, the manganese is added and the decomposition is effected with dilute sulphuric acid. I prefer to conduct the decomposition in the apparatus figured p. 294, collecting the carbonic acid in a weighed soda-lime tube.

As the manuring value of a sample of guano may be estimated, with sufficient accuracy, from the phosphoric acid and nitrogen which it con-

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some time. In the first case, the solution contains much oxalate and little phosphate, together with some sulphate of ammonia; in the second case, the oxalate of ammonia is more or less completely replaced by phosphate of ammonia, the oxalic acid having combined with lime in the residue. The cause of this deportment is that phosphate of lime, although when in contact with oxalate of ammonia and water alone it scarcely suffers any change, is very soon converted into oxalate of lime, with formation of phosphate of ammonia, when sulphate of ammonia (or chloride of ammonium) is also present. The sulphate of ammonia renders the phosphate of lime somewhat soluble, the dissolved part is at once precipitated by the oxalic acid, and the sulphate of ammonia is thus enabled to act afresh upon the phosphate of lime.

tains, the analysis is often considerably shortened, and confined to the following processes:—

a. Determination of Water (see 1).

b. Determination of Ash (see 2).

c. Determination of Phosphoric Acid.—Mix 1 part (1 or 2 grm.) of the sample of guano with 1 part of carbonate of soda and 1 part of nitrate of potassa; ignite cautiously, dissolve the residue in hydrochloric acid, evaporate to dryness on the water-bath, treat with hydrochloric acid and water, filter, add ammonia to the filtrate to alkaline reaction, then acetic acid until the phosphate of lime is redissolved, and lastly—without previously filtering off the very trifling precipitate of phosphate of sesquioxide of iron—acetate of sesquioxide of uranium, and determine the phosphoric acid as directed p. 272, *c*.

d. Determination of Nitrogen, after § 185.—As mixing the guano in the mortar with soda-lime would be attended with escape of an appreciable amount of ammonia, it is advisable to effect this operation in the combustion tube, with the aid of a wire (comp. pp. 426—8).

C. Analysis of Bone Dust

§ 234.

There are three sorts of bone dust.

I. The powder obtained by the grinding of more or less fresh bones, which is generally very coarse.*

II. The powder obtained by the grinding of more or less decayed bones.

III. The powder of bones which, previous to the operation of grinding, have been submitted to the action of boiling water, or high-pressure steam.

I. is very coarse, and contains a relatively large proportion of fat and of gelatigenous matter. II. is considerably poorer in organic substances. III. is much finer than I. and II.; it contains hardly any fat, and is somewhat poorer in gelatigenous matter.

I. Examine the powder, in the first place, by careful inspection, sifting, and elutriation, to ascertain the degree of comminution, and the presence of foreign matters.

2. *Determination of the Water.*—Dry a sample at 125°.

3. *Total amount of fixed Constituents.*—Ignite, about 5 grm., with access of air, until the ash appears white; moisten with carbonate of ammonia, dry, ignite gently, and weigh the residue.

4. *Fixed Constituents singly.*—Treat the ash of 3 with dilute hydrochloric acid, filter off the insoluble portion (sand, &c.), and determine the sesquioxide of iron, lime, magnesia, chloride of sodium, and phosphoric acid in the solution as directed § 232, 4.

5. *Nitrogen.*—Ignite 0·5—0·8 grm. with soda-lime (§ 185).

6. *Fat.*—Exhaust 5 grm. of the sample (ground as finely as possible), by boiling with ether, and dry the residue at 125°. The loss of weight *minus* the moisture found in 2, shows the amount of fat. By way of

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* ["Flour of bone" obtained from fresh bones contains several per cent. of common salt to preserve it from putrefaction.]

control, the ether may be distilled off, and the residual fat weighed, care being taken to leave no water under the fat.

7. Deduct from the total weight the sum of the fixed constituents, carbonic acid, water, and fat; the difference expresses the *gelatigenous matter*.

8. Determine the *carbonic acid* after p. 293 *e*.

D. ANALYSIS OF SUPERPHOSPHATE.

§ 235.

Substances which contain basic phosphate of lime in a difficultly soluble condition, are often converted into so-called *superphosphate*, for the purpose of rendering the phosphoric acid soluble, and consequently more readily accessible to plants. This is done by subjecting them to the action of a certain quantity of acid, usually sulphuric (occasionally associated with hydrochloric), by which sulphate of lime (and chloride of calcium), acid phosphate of lime and phosphoric acid are formed.*

The following bodies are employed for the preparation of superphosphate, viz., spent bone-black from sugar refineries, coprolite, apatite, phosphorite, Baker guano, precipitated basic phosphate of lime from glue works, and, more rarely, bone dust.

As it is unusual to employ enough acid to set the whole of the phosphoric acid free, the superphosphates generally consist of mixtures of sulphate of lime (and chloride of calcium), basic phosphate of lime, phosphate of sesquioxide of iron, phosphoric acid, and water. Carbon or organic matter (containing nitrogen) is frequently also present. Their quality is very variable, according to the raw material employed and the method of treatment, but they all agree in this, that they consist of substances (*a*) readily soluble in water, (*b*) difficultly soluble in water, and (*c*) insoluble in water.

Before we can judge of the value of a superphosphate it is absolutely necessary to know, not merely the quantity of the constituents, but how they are combined and how they deport themselves with solvents; hence the analysis becomes somewhat complicated.

1. Dry about 3 grm. of the sample at 160—180°. The loss of weight expresses *a*, the *moisture*; *b*, the *water of the sulphate of lime*.

2. Triturate 10 grm. of the undried superphosphate in a dish with cold water by the aid of a pestle, till all the lumps are completely broken down, allow to settle, pour off the clear supernatant fluid through a filter, and repeat the extraction with cold water, till the fluid no longer shows acid reaction. Dilute the aqueous solution so obtained to 500 c. c., and dry the residue at about 100°.

3. Divide the *aqueous solution*, which generally appears yellow from the presence of organic matter, into 4 portions, viz., *a*, *b*, and *c*, of 100 c. c. each, and *d*, of 200 c. c.

a. Evaporate in a platinum dish, adding, after some time, cautiously, thin milk of lime just to distinct alkaline reaction; proceed with the evaporation, dry the residue at 180°, and weigh; ignite the weighed residue and weigh again: the difference between the two weighings expresses the quantity of *organic matter* in the aqueous solution. Boil the residue with pure lime-water, then with water, filter, precipitate the sulphuric acid from the filtrate by addition of a little chloride of barium, then the baryta and lime by carbonate of ammonia, and determine the *alkalies* as chlorides according to p. 345, **15**.

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* Comp. Reinh. Weber, Pogg. Annal. 109, 505.

b. Precipitate with chloride of barium, and determine the *sulphuric acid* in the usual way (§ 132, I., 1).

c. Serves for the determination of any *hydrochloric acid* after § 141. Organic matter, if present in large quantity, is destroyed as in *d.*

d. Add an excess of carbonate of soda and a little nitrate of potassa, and evaporate to dryness in a platinum dish. Ignite the residue gently, then soften with water, rinse into a beaker, add hydrochloric acid, and apply a gentle heat until complete solution is effected. Add to the clear fluid, ammonia, then acetic acid in excess; filter off the *phosphate of sesquioxide of iron*, and divide the filtrate into two equal portions. Determine in one the *phosphoric acid** with uranium solution either gravimetrically, after p. 272, *c*, or by the volumetric method, p. 274. Estimate in the other portion the *lime* and *magnesia* as directed p. 349, **29.**

4. Transfer the residue of 2 to a weighed platinum dish, add the ash of the filter, dry at 180°, and weigh. The weight expresses the total amount of substances insoluble in water. Now ignite gently, with access of air, until the whole of the organic matter and charcoal is burnt; the loss of weight indicates the amount of these latter.

5. Boil the residue of 4 with dilute hydrochloric acid; after boiling for some time, dilute with water, filter, and dilute the filtrate by means of the washing water to $\frac{1}{4}$ litre; treat the insoluble residue as directed in 7.

6. Of the hydrochloric acid solution obtained in 5, measure off two portions, one of 50, the other of 100 c. c. In the former determine the *sulphuric acid*, in the latter the *phosphate of sesquioxide of iron* (if present), *lime*, *magnesia*, and *phosphoric acid*,* as in 3, *b* and *d.*

7. Dry, ignite, and weigh the insoluble residue of 5. It generally consists only of *sand*, *clay*, and *silicic acid*. To make quite sure, however, boil with concentrated hydrochloric acid; should some more sulphate of lime be dissolved, determine the amount of this in the solution.

8. Lastly, determine the *nitrogen* in 0·8—1 grm. of the superphosphate (§ 185). In arranging the results, it must not be forgotten that the nitrogen is part of the organic matter previously determined.

9. Should the superphosphate contain an ammonia salt, determine the ammonia as directed p. 157, 3, *a.*

As regards the statement of the results, the following plan presents a very good bird's-eye view of the analysis:—

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*[Many superphosphates contain considerable quantities of phosphates of iron and alumina which are to some extent extracted by water. In such cases the above method will not give good results, but both the soluble and insoluble phosphoric acid must be separated by means of molybdic solution, either from the original solution in water or hydrochloric acid, or from the acetate of ammonia precipitate. See p. 271.]

			Anhydrous phosphoric acid.	Nitrogen.
Constituents readily soluble in water.	Hydrate of phosphoric acid ($3\,HO, PO_5$).	16·15	11·70	—
	Lime, Magnesia, Sesquiox. iron, Potash, dissolved by, or combined with, the free phosphoric acid	0·50	—	—
Constituents difficultly soluble in water.	Sulphate of lime (CaO, SO_3+2 aq.) ……	42·00	—	—
Constituents soluble in acids.	Phosphoric acid……………………	2·19	2·19	—
	Lime, Magnesia, Sesquiox. iron, combined with the phosphoric acid to more or less basic salts	1·01	—	—
Constituents insoluble in acids.	Clay and sand……………………	2·49	—	—
Organic constituents and carbon……………………		6·51	—	0·41
Moisture ……………………………………		29·15	—	—
		100·00	13·89	0·41

It will be seen that we calculate the sulphuric acid found in solution and residue into sulphate of lime, and add both the quantities together. The residual quantities of lime in the solution and the residue, *i.e.*, the portions not combined with sulphuric acid, are then put down as above. If the superphosphate was prepared with sulphuric and hydrochloric acids, the chlorine in the aqueous solution is to be calculated into chloride of calcium, and the lime corresponding thereto + the lime combined with sulphuric acid is to be deducted from the total quantity found in the aqueous solution. The remainder is then to be put down as dissolved by, or combined with, phosphoric acid.

[ABRIDGED ANALYSIS OF SUPERPHOSPHATES.

§ 236.

For most ordinary purposes it is sufficient to estimate on 1 grm.—

A. *Water expelled at* 100° by drying in water-bath.

B. *Organic and other volatile matters* by gentle ignition and incineration of A until carbon is mostly consumed.

C. *Sand and insoluble matters* by treatment of the residue of B with nitric acid.

D. *Total phosphoric acid* in ⅕ of the solution C by means of molybdic solution, when iron and alumina are present in quantities of over ½ per cent.; or, in absence of iron and alumina, by titration with standard uranium solution.

E. *Soluble phosphoric acid* by treating 10 grm. as directed above, § 235, 2 and estimating phosphoric acid in aliquot parts (50 c. c.) of the solution, with uranium or molybdic solution—see foot-note p. 549.

F. *Nitrogen* in 0·5 grm. by combustion with soda lime, § 185.

More important than determining the quantities of lime, magnesia, &c., is a study of the *condition* of the phosphates insoluble in water, and of the nitrogen. The former are much more valuable as fertilisers when existing as bone-earth than when composed of crystallized apatite or compact coprolite. The latter in gelatine or blood is very active, while in the form of leather shavings it is nearly inert.]

E. Analysis of Bone Black.

§ 237.

Bone black is extensively employed for decolorizing and removing the lime from the juice in the preparation of beetroot sugar, and in the refining of cane sugar. When freshly prepared it consists of a mixture of bone earth with 7—10 per cent. of carbon, but on use it takes up lime, coloring matter, mucilage, &c., from which it is freed during the process of reanimation, by washing, treating with hydrochloric acid, washing again, drying and igniting. When at last it is thoroughly used up, or "spent," it passes into the manure manufactories, and is then generally applied to the preparation of superphosphate. As the bone black is much altered and contaminated by the numerous operations through which it passes, its value varies very considerably, and can only be estimated by analysis. Again, before being submitted to the revivifying process, bone black always requires testing, in order that it may be known how much hydrochloric acid it is necessary to employ; in this case we have to find the quantity of the lime which is not combined with phosphoric acid (and which is usually present in the form of carbonate of lime).

We describe, in the first place, the ordinary method of analyzing bone black, and then a process for determining the carbonate of lime.

General Process.

1. Dry 2—3 grm. at 160—180°. The loss of weight indicates the *moisture*.

2. Dissolve 5 grm. in the flask *a* of the apparatus figured p. 293, and determine the *carbonic acid* as there described.

3. Filter the solution through a weighed filter, wash the residue, dry at 100°, and weigh. This will give you the sum of the charcoal, the insoluble organic matter and the mineral impurities insoluble in hydrochloric acid (sand and clay). Now ignite the dried filter with access of air. This will give you the *sand* and *clay* as the residue. The *charcoal* and insoluble *organic matter* is found by difference.

4. Make the filtrate obtained in 3 up to 250 c. c. and determine in 100 c. c. *iron, lime, magnesia, and phosphoric acid*, in 50 c. c. the *sulphuric acid* that may be present, and in the last 100 c. c. the *alkalies* possibly present according to § 232, *b*. p. 544.

5. Dissolve another weighed portion of the substance in dilute nitric acid, dilute and determine in the filtrate the *hydrochloric acid* possibly present.

Process for Determining the Carbonate of Lime or the Carbonate of Lime and Caustic Lime.

§ 238.

For determining *carbonate of lime* 3 grm. of the bone black are dried and *powdered as finely as possible*. Estimate carbonic acid according to *g*, p. 298, from this calculate the carbonate of lime. If a bone black contains hydrate of lime, moisten a portion weighed off in a porcelain dish with 10—20 drops of carbonate of ammonia, evaporate to dryness, heat the residue somewhat more strongly (but by no means to ignition), and transfer without loss to the decomposing bottle. Calculate as before; the excess over the first estimation is carbonate equivalent to the caustic lime present.

§ 239.

19. [ANALYSIS OF COAL AND PEAT.

For technical purposes, estimations of moisture, ash, coke, and volatile matters usually suffice. Determination of sulphur is less frequently required, and ultimate analysis is only resorted to in special cases.

a. Moisture. The finely pulverized coal (3—5 grm.) is heated to 110—115° for an hour or more, or until it ceases to lose weight (see § 29). Many bituminous coals gain weight after a time from oxidation of sulphides or hydro-carbons (WHITNEY). According to HINRICHS,* drying the coal for one hour effects the maximum loss.

b. Coke and *volatile matters.* The dried coal of *a* is sharply heated in a closed platinum, or, in presence of sulphides, in a porcelain crucible as long as combustible matters issue from it. It is then cooled quickly. The loss is set down as volatile matters. The residue, less the ash, is coke.

c. Ash. The residue of *b* is incinerated in a crucible placed aslant.

d. Carbon and *hydrogen* are determined by combustion with chromate of lead and bichromate of potash, § 177.

e. Nitrogen is estimated according to § 185.

f. Sulphur is determined as directed § 219, *c*. p. 515, but the evaporation with hydrochloric acid is omitted, and the sulphate of baryta, after decanting the supernatant liquid upon a filter, is boiled up two or three times with dilute solution of acetate of ammonia, to free it from adhering salts. STORER AND PEARSON.]

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* Chemical News, 19, 282.

III. ANALYSIS OF ATMOSPHERIC AIR.

§ 240.

In the analysis of atmospheric air we usually confine our attention to the following constituents: oxygen, nitrogen, carbonic acid, and aqueous vapor. It is only in exceptional cases that the exceedingly minute quantities of ammonia and other gases—many of which may be assumed to be always present in infinitesimal traces—are also determined.

It does not come within the scope of the present work to describe all the methods which have been employed in the capital investigations made in the last few years by BRUNNER, BUNSEN, DUMAS and BOUSSINGAULT, REGNAULT and REISET, and others. To these methods we are indebted for a more accurate knowledge of the composition of our atmosphere, and excellent descriptions of them will be found in the works below.*

I confine myself to those methods which are found most convenient in the analysis of the air for medical or technical purposes.

A. DETERMINATION OF THE WATER AND CARBONIC ACID.

§ 241.

It was formerly the custom to effect these determinations by BRUNNER'S method, which consisted in slowly drawing, by means of an aspirator, a measured volume of air through accurately weighed apparatuses filled with substances having the property of retaining the aqueous vapor and the carbonic acid, and estimating these two constituents by the increased weights of the apparatuses.

Fig. 102 represents the arrangement recommended by REGNAULT.

The vessel *V* is made of galvanized iron, or of sheet zinc; it holds from 50 to 100 litres, and stands upon a strong tripod in a trough large enough to hold the whole of the water that *V* contains. At *a* a brass tube *c*, with stopcock, is firmly fixed in with cement. Into the aperture *b*, which serves also to fill the apparatus, a thermometer reaching down to the middle of *V* is fixed air-tight by means of a perforated cork soaked in wax.

The efflux tube, *r*, which is provided with a cock, is bent slightly upward, to guard against the least chance of air entering the vessel from below. The capacity of the vessel is ascertained by filling it completely with water, and then accurately measuring the contents in graduated vessels. The end of the tube *c* is connected air-tight with *F*, by means of a caoutchouc tube; the tubes *A*—*F* are similarly connected with one another. *A*, *B*, *E*, and *F* are filled with small pieces of glass moistened with pure concentrated sulphuric acid, C and D with moist hydrate of lime.* Finally, A is also connected with a long tube leading to the place from which the air intended for analysis is to be taken. The corks of the tubes are coated over with sealing-wax. The tubes A and B are intended to withdraw the moisture from the air; they are weighed together. C, D, and E are also weighed jointly. C and D absorb the carbonic acid; E the aqueous vapor which may have been withdrawn from the hydrate of lime by the dry air. F need not be weighed; it simply serves to protect E against the entrance of aqueous vapor from V.

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* Ausführliches Handbuch der analytischen Chemie von H. Rose, II. 853; Graham-Otto's ausführliches Lehrbuch der Chemie, Bd. II. Abth. 1, S. 102 *et seq.*; Handwörterbuch der Chemie von Liebig, Poggendorff und Wöhler, 2 Aufl. Bd. II. S. 431 *et seq.*; and Bunsen's Gasometry.

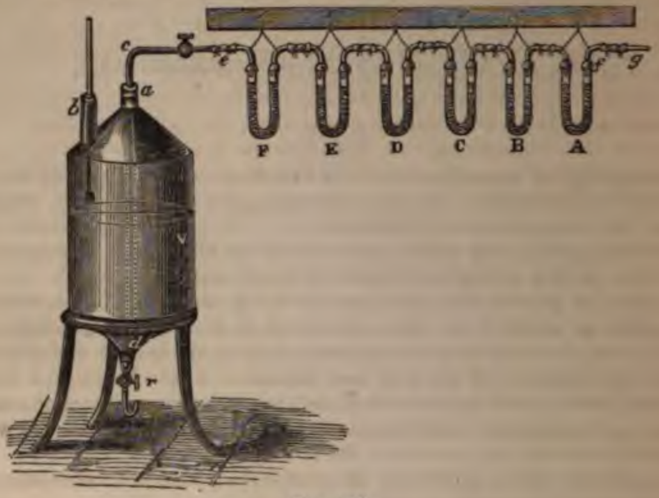

Fig. 102.

The aspirator is completely filled with water; c is then connected with F, and thus with the entire system of tubes; the cock r is opened a little, just sufficiently to cause a slow efflux of water. As the height of the column of water in V is continually diminishing, the cock must from time to time be opened a little wider, to maintain as nearly as possible a uniform flow of water. When V is completely emptied, the height of the thermometer and that of the barometer are noted, and the tubes A and B, and C, D, and E weighed again.

As the increase of weight of A and B gives the amount of water, that of C, D, and E, the amount of carbonic acid, in the air which has passed through them; and as the volume of the latter (freed from water and carbonic acid) is accurately known from the ascertained capacity of *V*;* the calculation is in itself very simple; but it involves, at least in very accurate analyses, the following corrections:—

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* With regard to C and D, I have returned to lime, preferring it to pumice saturated with solution of potash, because, as Hlasiwetz (Chem. Centralbl. 1856, 575) has shown, the solution of potash absorbs not only carbonic acid, but also oxygen. Indeed, H. Rose had previously made a similar observation. With respect to the other tubes, I prefer the concentrated sulphuric acid to chloride of calcium as the absorbent for water (see Pettenkofer, Sitzungsber. der bayer. Akad. 1862, II. Heft 1, S. 59). Hlasiwetz's statement, that concentrated sulphuric acid also takes up carbonic acid, I have found to be unwarranted. Chloride of calcium does not dry the air completely, and, besides, Hlasiwetz says that when it is used a trace of chlorine is carried away corresponding to the amount of ozone in the air (op. cit. p. 517).

α. Reduction of the air in *V*, which is saturated with aqueous vapor, to dry air; since the air which penetrates through *c* is dry (see § 195, *γ*).

β. Reduction of the volume of dry air so found to 0°, and 760 mm. (§ 195, *α* and *β*).

When these calculations have been made, the weight of the air which has penetrated into *V* is readily found from the datum in Table V. at the end of the volume; and as the carbonic acid and water have also been weighed, the respective quantities of these constituents of the air may now be expressed in per-cents by weight, or, calculating the weights into volumes, in per-cents by measure.

Considering the great weight and size of the absorption apparatus, in comparison to the increase of weight by the process, at least 25,000 c. c. of air must be passed through; the air inside the balance-case must be kept as dry as possible by means of a sufficient quantity of chloride of calcium, and the apparatus left for some time in the balance-case, before proceeding to weigh. Neglect of these measures would lead to considerable errors, more particularly as regards the carbonic acid, the quantity of which in atmospheric air is, on an average, about 10 times less than that of the aqueous vapor (comp. HLASIWETZ, *loc. cit.*).

For the *exact determination of the carbonic acid* one of the following methods is far better suited:—

a. Process suggested by FR. MOHR, *applied and carefully tested by* H. v. GILM.† VON GILM employed in his experiments an aspirator holding at least 30 litres, which was arranged like that shown in fig. 102, but had a third aperture, bearing a small manometer. The air was drawn through a tube, 1 metre long, and about 15 mm. wide; this tube was drawn out thin at the upper end, and at the lower end bent at an angle of 140—150°. It was more than half filled with coarse fragments of glass and perfectly clear baryta water, and fixed in such a position that the long part of it was inclined at an angle of 8—10° to the horizontal. A narrow glass tube, fitted into the undrawn-out end of the tube by means of a cork, served to admit the air. Two small flasks, filled with baryta water, were placed between the absorption tube and the aspirator; these were intended as a control, to show that the whole of the carbonic acid had been retained. When about 60 litres of air had slowly passed through the absorption tube, the carbonate of baryta formed was filtered off out of contact of air, and the tube as well as the contents of the filter washed, first with distilled water saturated with carbonate of baryta, then with pure boiled water. The carbonate of baryta in the filter and in the tube was then dissolved in dilute hydrochloric acid, the solution evaporated to dryness, the residue gently ignited, and the chlorine of the chloride of barium determined as directed § 141, *b*, *α*. 1 eq. chlorine represents 1 eq. carbonic acid. It is obvious that one may also determine the baryta in the hydrochloric acid solution by precipitating with sulphuric acid. For filtering the carbonate of baryta, v. GILM employed a double funnel (fig. 103); the inner cork has, besides the perforation through which the neck of the funnel passes, a lateral slit, which establishes a communication between the air in the outer funnel and the air in the bottle.

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* Or from the quantity of water which has flown from *V*, as the experiment may be altered in this way, that a portion only of the water is allowed to run out, and received in a measuring vessel.

† Chem. Centralbl. 1857, 760.

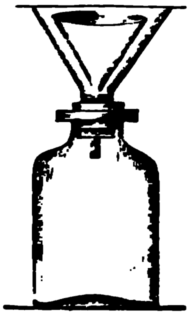

Fig. 103.

As, with the absorption apparatus arranged as described, the air has to force its way through a column of fluid, the manometer is required to determine the actual volume of the air: the height indicated by this instrument being deducted from the barometric pressure observed during the process.

Fr. Mohr[*] now recommends as the absorbent fluid a solution of baryta in potash. This is prepared by dissolving crystals of baryta in weak solution of potash with the aid of heat, and filtering off the carbonate of baryta, which invariably forms in small quantity. The clear filtrate is accordingly saturated with carbonate of baryta. Mohr now leaves out the fragments of glass.

This method afforded v. Gilm very harmonious results. Nevertheless, it involves one source of error. If clear baryta water is passed through paper with the most careful possible exclusion of air, and the filter is washed till the washings are free from baryta, and dilute hydrochloric acid is then poured upon the filter, and the filtrate thus obtained is evaporated, a small quantity of chloride of barium will be left, showing that a little baryta was kept back by the paper. Al. Müller[†] has already called attention to the capacity of filter paper for retaining baryta.

b. M. Pettenkofer's *process.*[‡]

a. Principle and Requisites.—A known volume of air is made to act upon a definite quantity of standard baryta water (standardized by oxalic acid solution), in such manner that the carbonic acid is completely bound by the baryta. The baryta water is then poured out into a cylinder, and allowed to deposit with exclusion of air, a part of the clear fluid is then removed, and the baryta remaining in solution is determined. The difference between the oxalic acid required for a certain quantity of baryta water before and after the action of the air, represents the carbonate of baryta formed, and consequently the carbonic acid present.

Two kinds of baryta water are used: one contains 21 grm. and the other 7 grm. crystallized hydrate of baryta[‖] in the litre; these serve for the determination of larger and smaller quantities of carbonic acid

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[*] Lehrbuch der Titrirmethode, 2d ed. 446.

[†] Journ. f. prakt. Chem. 83, 384.

[‡] Abhandl. der naturw. u. techn. Commission der k. bayer. Akad. der Wiss. II 1; Ann. d. Chem. u. Pharm. II. Supplem. Bd. p. 1.

[‖] The hydrate of baryta must be entirely free from caustic potash, and soda, the smallest quantities of which render the volumetric estimation in the presence of carbonate of baryta impossible, since the neutral alkaline oxalates decompose the alkaline earthy carbonates. When a trace even of carbonate of baryta is suspended in the fluid—and this is always the case when a baryta water which has been used for the absorption of carbonic acid is not filtered—the reaction continues alkaline if the smallest trace of potash or soda is present, because the alkaline oxalate formed immediately enters into decomposition with the carbonate of baryta. A fresh addition of oxalic acid converts the alkaline carbonate again into oxalate, and the fluid is for a moment neutral, till, on shaking with respectively. 1 c. c. of the stronger corresponds to about 3 mgrm. carbonic acid, of the weaker 1 c. c. corresponds to about 1 mgrm.*

The oxalic acid solution which serves for standardizing the baryta water contains 2·8636 grm. cryst. oxalic acid in 1 litre. 1 c. c. corresponds to 1 mgrm. carbonic acid. The baryta water is standardized as follows:—transfer 30 c. c. of it to a flask, and then run in the oxalic acid from a MOHR's burette with float; shake the fluid from time to time, closing the mouth of the flask with the thumb. The vanishing point of the alkaline reaction is ascertained with delicate turmeric paper.† As soon as a drop of the fluid placed on the paper does not give a brown ring, the end is attained. If you were obliged, in the first experiment, to take out too many drops for testing with turmeric paper, consider the result as only approximate, and make a second experiment, adding at once the whole quantity of oxalic acid to within 1 or $\frac{1}{2}$ c. c. and then beginning to test with paper. A third experiment would be found to agree with the second to $\frac{1}{10}$ c. c. The reaction is so sensitive that all foreign alkaline matter, particles of ash, tobacco smoke, &c., must be carefully guarded against.

β. *The actual Analysis.*—This may be effected in two different ways.

aa. Take a perfectly dry bottle, of about 6 litres capacity, with well-fitting ground glass stopper, and accurately determine the capacity; fill the bottle, by means of a pair of bellows, with the air to be analyzed; add 45 c. c. of the dilute standard baryta water, and cause the baryta water to spread over the inner surface of the bottle, by turning the latter about, but without much shaking. In the course of about $\frac{1}{2}$ an hour the whole of the carbonic acid is absorbed. Pour the turbid baryta water into a cylinder, close securely, and allow to deposit; then take out, by means of a pipette, 30 c. c. of the clear supernatant fluid, run in standard oxalic acid, multiply the volume used by 1·5 (as only 30 c. c. of the original 45 are employed in this experiment), and deduct the product from the c. c. of oxalic acid used for 45 c. c. of the fresh baryta water; the difference represents the quantity of baryta converted into carbonate, and consequently the amount of the carbonic acid. If the air is unusually rich in carbonic acid, the concentrated baryta water is employed.

bb. Pass the air through a tube or through two tubes containing measured quantities of standard baryta water and finish the experiment as in *aa.* For passing a definite quantity of air we should generally employ an aspirator (p. 554); PETTENKOFER in his experiments with the respiration apparatus forced the air by means of small mercurial pumps first

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air, the carbonic acid escapes, and any carbonate of baryta still present converts the alkaline oxalate again into carbonate. To test a baryta water for caustic alkali, determine the alkalinity of a perfectly clear portion, and then of a portion that has been mixed with a little pure precipitated carbonate of baryta. If you use more oxalic acid in the second than in the first experiment, caustic alkali is present, and some chloride of barium must be added to the baryta water before it can be used.

* [The baryta water is kept in a bottle under a thin stratum of kerosene (MOHR). It is drawn off through a syphon supported in the stopper, the outer leg of which is recurved upwards and closed with a bit of rubber tube and clip. By having this leg of the syphon sufficiently long the burette may be filled by inserting its delivery end in the rubber tube and opening both clips.]

† Prepared with lime-free Swedish filter paper, and tincture of turmeric. The spirit used in making the latter must be free from acid. Dry the paper in a dark room, and keep it protected from the light. It is lemon yellow.

through the tubes, and then through an apparatus for measuring the gas. The form and arrangement of the tubes is illustrated by fig. 104. Two such tubes were used; the first was 1 metre, the second ·3 metres long; they were filled with baryta water—the former with the stronger solution, the latter with the weaker. The air is introduced through the short limbs of the tubes, and is carried beyond the bends by a narrow flexible tube, and the glass tubes themselves are so inclined that the bubbles of air move on with the necessary rapidity without uniting. The motion of the gas bubbles keeps up a constant mixing of the baryta water.

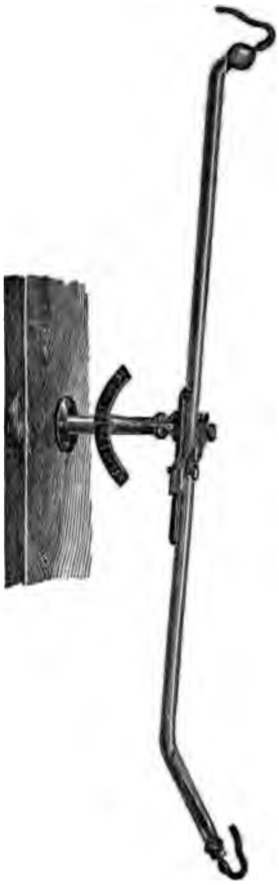

Fig. 104.

B. Determination of the Oxygen and Nitrogen.

§ 242.

The method I shall give is that proposed by v. Liebig.* It is based upon the observation made by Chevreul and Döbereiner, that pyrogallic acid, in alkaline solutions, has a powerful tendency to absorb oxygen.

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* Annal. d. Chem. u. Pharm. 77, 107.

1. A strong measuring tube, holding 30 c. c., and divided into $\frac{1}{5}$ or $\frac{1}{10}$ c. c., is filled to $\frac{2}{3}$ with the air intended for analysis. The remaining part of the tube is filled with mercury, and the tube is inverted over that fluid in a tall cylinder, widened at the top.

2. The volume of air confined is measured (§ 12). If it is intended to determine the carbonic acid —which can be done with sufficient accuracy only if the quantity of the acid amounts to several per-cents—the air is dried by the introduction of a ball of chloride of calcium before measuring. If it is not intended to determine the carbonic acid, this operation is omitted. A quantity of solution of potassa of 1·4 sp. gr. (1 part of dry hydrate of potassa to 2 parts of water), amounting to from $\frac{1}{40}$ to $\frac{1}{50}$ of the volume of the air, is then introduced into the measuring tube by means of a pipette with the point bent upwards (fig. 105), and spread over the entire inner surface of the tube by shaking the latter; when no further diminution of volume takes place, the decrease is read off. If the air has been dried previously with chloride of calcium, the diminution of the volume expresses exactly the amount of carbonic acid contained in the air; but if it has not been dried with chloride of calcium, the diminution in the volume cannot afford correct information as to the amount of the carbonic acid, since the strong solution of potassa absorbs aqueous vapor.

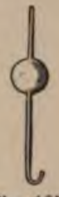

Fig. 105.

3. When the carbonic acid has been removed, a solution of pyrogallic acid, containing 1 grm. of the acid * in 5 or 6 c. c. of water, is introduced into the same measuring tube by means of another pipette, similar to the one used in 2 (fig. 105); the quantity of pyrogallic acid employed should be half the volume of the solution of potassa used in 2. The mixed fluid (the pyrogallic acid and solution of potassa) is spread over the inner surface of the tube by shaking the latter, and, when no further diminution of volume is observed, the residuary nitrogen is measured.

4. The solution of pyrogallic acid mixing with the solution of potassa of course dilutes it, causing thus an error from the diminution of its tension; but this error is so trifling that it has no appreciable influence upon the results; it may, besides, be readily corrected, by introducing into the tube, after the absorption of the oxygen, a small piece of hydrate of potassa corresponding to the amount of water in the solution of the pyrogallic acid.

5. There is another source of error in this method; viz., on account of a portion of the fluid always adhering to the inner surface of the tube, the volume of the gas cannot be read off with absolute accuracy. In comparative analyses, the influence of this defect upon the results may be almost entirely neutralized, by taking nearly equal volumes of air in the several analyses.†

6. Notwithstanding these sources of error, the results obtained by this method are very accurate and constant. In eleven analyses which v. Liebig reports, the greatest difference in the amount of oxygen found was between 20·75 and 21·03. The numbers given express the actual and uncorrected results.

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* Liebig has described a very advantageous method of preparing pyrogallic acid. See Annal. d. Chem. u. Pharm. 101, 47.

† Bunsen employs for the absorption of oxygen a papier-mâché ball saturated with a concentrated alkaline solution of pyrogallate of potassa, which he introduces into the gaseous mixture attached to a platinum wire. By adopting this proceeding, the source of error mentioned in 5 is avoided. See also Russell, Jour. Chem. Soc. 1868, pp. 130, 131.

PART III.

EXERCISES FOR PRACTICE.

EXERCISES FOR PRACTICE.

The principal point kept in view in the selection of these exercises has been that most of them, and more particularly the first, should permit an exact control of the results. This is of the utmost importance for students, since a well-grounded self-reliance is among the most indispensable requisites for a successful pursuit of quantitative investigations, and this is only to be attained by ascertaining for one's self how near the results found approach the truth.

Now a rigorously accurate control is practicable only in the analysis of pure salts of known composition, or of mixtures composed of definite proportions of pure bodies. When the student has acquired, in the analysis of such substances, the necessary self-reliance, he may proceed to the analysis of minerals or products of industry in which such rigorous control is unattainable.

The second point kept in view in the selection of these exercises, has been to make them comprise both the more important analytical methods and the most important bodies, so as to afford the student the opportunity of acquiring a thorough knowledge of every branch of quantitative analysis.

Organic analysis offers less variety than the analysis of inorganic substances; the exercises relating to the former branch are therefore less numerous than those relating to the latter.

I would advise the student to analyze the same substance repeatedly, until the results are quite satisfactory. [It is a good habit always to carry on together duplicate analyses. It requires but little more time to make two analyses than to make one, and the operator's experience is thus very economically doubled.]

It is by no means necessary for the student to go through the whole of these examples; the time which he may require to attain proficiency in analysis depends, of course, upon his own abilities. One may be a good analyst without having tried *every* method, or determined *every* body. A few substances *well* analyzed yield more profit than can be obtained from going over many processes in a superficial manner.

Finally, the student is warned against prematurely attempting to discover new methods; he should wait until he has attained a good degree of proficiency in general chemistry, and more particularly in practical analysis.

EXERCISES.

A. SIMPLE DETERMINATIONS IN THE GRAVIMETRIC WAY, INTENDED TO PERFECT THE STUDENT IN THE PRACTICE OF THE MORE COMMON ANALYTICAL OPERATIONS.

[WE give here, in the first place, quite full details of all the steps in the estimation of chlorine in chloride of sodium, including the preparation of this salt in a state of purity. This, it is hoped, will relieve much of the perplexity which the beginner must at first experience in making out a scheme of operations from the various separate paragraphs where the processes are described. The student should not fail, however, to study carefully the chapter on operations while carrying on the analysis, nor to examine every reference.

1. CHLORIDE OF SODIUM.

Preparation.—Dissolve 150 grm. of clean crystallized carbonate of soda in hot water, place a small bit of litmus paper in the solution, add pure hydrochloric acid to acid reaction, and evaporate in a porcelain dish to dryness, whereby silica becomes insoluble. If the dry residue has a yellow tinge, which is due to iron, raise the heat somewhat until the residue is brown or black in color and no acid odor is perceptible when it is breathed on. This treatment converts soluble sesquichloride of iron into insoluble oxychloride. Dissolve the residue in hot water, filter, and evaporate the solution, contained in a beaker, at a temperature somewhat below the boiling point, until there remains a small quantity of liquid above the crystals of salt. Pour off this mother liquor, rinse the crystals repeatedly with small quantities (their own bulk) of cold water until the rinsings give but a very slight * reaction for sulphuric acid with chloride of barium.

A portion † of the salt thus obtained is crushed to a coarse powder, heated in a covered crucible until it ceases to decrepitate, but not to fusion, and preserved in a weighing tube (like a small test tube, but not flared at the mouth) that is closed with a soft, well-fitting, and smooth cork.

ESTIMATION OF CHLORINE.

1. *Weighing out the substance.*—The tube containing the prepared salt is wiped, if need be, from dust. The cork is taken out, and by means of a bit of thin paper, or a clean linen handkerchief, any particles

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* It is not needful for ordinary quantitative purposes that a salt should be so free from foreign matters that the latter cannot be detected by sensitive reagents, and for the reason that it is not possible to collect and weigh the minute traces which are thus indicated.

† Pure chloride of sodium is needed in other analyses, and the chief part of what is thus prepared should be carefully bottled and reserved for future use.

of salt adhering to the cork, and to the inside of the tube as far as the cork reaches, are removed. The cork is replaced, and the whole is weighed (see §§ 9 and 10), the weight being immediately recorded in the note-book. A clean beaker or assay-flask, of about 200 c. c. capacity, being ready, the weighing-tube is held over it and the cork carefully removed. A portion of substance is allowed to fall in the vessel, and, the cork being replaced, the tube is again counterpoised. If two to three decigrammes have been emptied, the operator is ready to proceed. If less, more should be transferred from the tube to the vessel. If more, or much more, it is better to begin anew, by weighing off another portion into another beaker or flask. In this manner weigh off two portions in separate vessels, so as to carry together duplicate analyses. Now affix a piece of gummed paper to each vessel, and label them to correspond with their designation in the note-book.

2. *Solution and precipitation.*—Dissolve the weighed portions, each in about 100 c. c. of cold distilled water, add a few drops of pure nitric acid, and, lastly, clear solution of nitrate of silver * until further addition no longer produces a precipitate.

Agitate the mixture well, but with care to avoid loss. This can be done by shaking, if a flask be in use, or by stirring with a glass rod, if a beaker be employed.

Set the vessel aside in a dark place, covered with paper or a watch-glass to exclude dust, and let stand for about 12 hours, or until the precipitate has subsided and the liquid above it is *perfectly* clear, then add a drop of nitrate of silver to make sure that the precipitation is complete (if not complete, add more solution of silver, and let stand again for some hours).

3. *Filtration.*—A filter is placed in a funnel at least ¼ inch deeper than itself, and moistened with water, at the same time being carefully pressed down so that its edges touch the glass at all points. The funnel being supported on a stand, a clean beaker or flask is put beneath it, and the operator proceeds to pour the liquid—on whose surface some particles of chloride of silver usually float—into the filter, leaving the bulk of the precipitate undisturbed. To do this without loss the following precautions may be regarded: *a.* Touch the edge or lip of the vessel with a very slight coat of tallow (a small bit of which is kept at hand under the edge of the work-table, and is applied with the finger). *b.* Pour slowly over the greased place, along a glass rod held nearly vertical, so directing the stream that it shall strike against the side, not into the vertex of the filter. *c.* When the filter is filled to within ¼ inch of the top discontinue the pouring, bringing the rod into the vessel containing the precipitate, after it has drained so that nothing will fall from it.

The pouring-rod may be simply straight, and an inch longer than the diagonal of the vessel, or, when it is desirable not to disturb a precipitate, it may be 3—4 inches long and bent syphon fashion so as to hang on the edge of a beaker or flask. In either case its end should be rounded by fusion, and those portions along which the liquid flows must not be handled.

The vessel containing the precipitate, as well as that which receives the filtrate, and likewise the funnel, should be kept *covered* as much as possible in all cases when nicety is required, to prevent access of dust, insects, &c.

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* Solution of a silver coin in nitric acid answers for this purpose as well as pure nitrate, provided it be clear and contain but little free acid.

The most convenient covers are large watch-glasses, but square plates of glass, or even cards, will generally answer. The receiving-vessel may also be protected by employing the filter-stand represented in fig. 34, p. 57.

The filtration of chloride of silver should be conducted without exposing it to strong light, whereby it is blackened, with loss of chlorine, p. 208.

d. When all, or nearly all, the liquid has passed the filter, it remains *to wash* and *to transfer* the precipitate.

These operations may be carried on as follows: pour about 100 c. c. of cold distilled water upon the precipitate, which mostly remains in the vessel where it was formed, and agitate vigorously, in order to break up and divide the lumpy chloride of silver, and bring every part of it perfectly in contact with the water.

When in a beaker, the agitation must be made with great caution, by means of a glass stirring-rod; when in a narrow-mouthed flanged flask, this may be tightly closed by a perfectly smooth cork (softened for the purpose by squeezing) and then shaken violently.

The water and precipitate are now poured together upon the filter, with the precautions before detailed. The last portions of the precipitate are removed from the beaker or flask by repeated rinsings, in which a wash-bottle like fig. 36, p. 59, may be conveniently employed.

Any portions of precipitate that adhere to the sides of the vessel too strongly to be removed by a stream from the wash-bottle must be *rubbed off*. For this purpose the feather is employed.

It is made from a goose-quill, by cutting off the extreme tip for an inch or so, and smoothly trimming away the beard, except a portion of one half-inch in length on the inside of the curve. The tubular part may be removed or not, to suit the depth of the dish which is to be washed.

The dish being wiped clean, externally, a little water is put in it, and, it being held up to the light, its whole interior surface is gently rubbed with the feather, then rinsed, rubbed again and rinsed, so long as careful inspection discovers any portions of adhering precipitate; finally, the feather is rinsed in a stream of water, the rinsings in each case being poured upon the filter.

The washing is now continued by help of the wash-bottle. A jet of cold water is directed, first, upon the interior of the funnel, just *above* the filter, then upon the edge of the filter itself. If thrown immediately against the paper, this is liable to be perforated. The stream of water is carried around the edge of the filter until the latter is nearly full, and the liquid is then allowed to drain off. This process is repeated until a portion of the wash-waters, collected to the depth of an inch in a test tube containing a drop of hydrochloric acid, give no turbidity of chloride of silver. When this is accomplished, the precipitate is washed down into the vertex of the filter. The funnel is then closely covered with paper (p. 62), labelled, allowed to drain thoroughly, and set away in a warm place for drying.

When the Bunsen pump is employed, read § 53 *c.* p. 77, and follow the directions on page 72, bottom; as to washing, see pp. 67 and 68.

5. *Drying the filter.* In public laboratories a heated closet is usually provided for drying filters. Its temperature should not exceed 100° C.

In default of such special arrangement, the drying may be effected over the register of a hot-air furnace, or over a common stove or kitchen range.

The funnel may also be supported on a retort-stand over a sheet of iron, which is heated beneath by a lamp, or may be placed at once in the water-bath. See pp. 62 and 79.

6. When the precipitate is perfectly dry we proceed to ignite it for *weighing*.

A small porcelain crucible (platinum must not be used) is cleaned, gently ignited, and when cool (after 15—20 minutes) weighed.

The work-table being clean, two small sheets of fine and smooth writing or glazed paper are opened and laid down side by side. The filter is removed from the funnel and carefully inverted upon one of the papers. The precipitate is loosened from the filter by squeezing and rubbing gently between the fingers, and when it has mostly separated the filter is lifted, reversed, and any portions of chloride of silver still adhering are loosened by rubbing its sides together. What is thus detached is poured or shaken out on the paper.

The filter is now spread out as a half-circle upon the other sheet of paper, and, beginning with the straight edge, is folded up into a narrow flattened roll, the two ends of which are then brought together. In this way those central portions of the filter to which particles of precipitate adhere are thoroughly enveloped by the exterior parts, so that in the subsequent burning nothing can easily escape.

The crucible being placed on the glazed paper, the filter is taken by the two free ends in a clean pincers or tongs, put to the flame of a lamp to set it on fire, and then held over the crucible until it is completely charred. It is then dropped into the crucible, and moistened with two or three drops of nitric acid. The crucible is covered and placed over a low flame until its contents are dry, it is then heated somewhat stronger, whereby the carbon is nearly or entirely consumed.

The crucible being allowed to cool, one more drop of nitric acid, and afterwards a drop of hydrochloric acid, is added to the residue, and it is heated cautiously, without the cover, until fumes cease to escape. This treatment with nitric acid serves to destroy carbon and convert any reduced silver to nitrate, which the hydrochloric acid in turn transforms into chloride. When the crucible is cool, it is placed again on the paper, and the precipitate is poured into it from the other sheet, the last particles being detached by cautious tapping with the fingers underneath, or by the use of a clean feather or camel's hair pencil.

The crucible is now put over a low flame and heated cautiously until the chloride of silver begins to fuse on the edges. It is then covered and let cool. When cold it is weighed. Read § 115, 1, and the references there made.

7. *Record and calculation of results.* The amount of chloride of silver is learned by subtracting from the total the joint weight of the crucible and filter-ash. The quantity of chlorine is obtained by multiplying the amount of chloride of silver by the decimal 0·24724. In order to compare results they are reduced to *per cent.* statements by the following proportion :—

Substance : chlorine in substance :: 100 : chlorine in 100; i.e. *per cent.*

The record may be made as follows: It is well to work out the calculations in full in the weight-book, as in case of mistake the data are at hand for revision.

		No. 1.		No. 2.
Na Cl and tube..........................		6·615		6·180
" " – substance...............		6·180		5·765
Substance............		·435		·415
Crucible, Ag Cl and Ash......		15·3630		14·3270
Cr...........................	14·298	14·2995	13·309	13·3105
Ash..........................	·0015		·0015	
Ag Cl......................		1·0635		1·0165
		0·24724		0·24724
		42540		40660
		21270		20330
		74445		71155
		42540		40660
		21270		20330
Cl.......................... =		·262939740		·251319460

·435) 26,29397 (60·44%
2610
1939
1740
1997

·415) 25,13194 (60·56%
2490
2319
2075
2444

	Found. No. 1.	Found. No. 2.	Calculated.
Chlorine	60·44	60·56	60·66

We have here employed the simplest arithmetical calculation. It is well to duplicate the calculation with help of the tables given in the Appendix. See pp. 462–4.

The first determination given above is not only fair for this method, but answers all ordinary purposes. The second is very good, though with care still closer accordance with theory can be easily attained.]

2. IRON.

Procure 10—15 grms. of fine bright pianoforte wire, cut it into lengths of about 0·3 grm. and keep it free from rust in a dry bottle.

Weigh, on a watch-glass, for each estimation, about 0·3 grm. of wire, and dissolve in hydrochloric acid, with addition of nitric acid. The acids are diluted with a little water.

The solution is effected by heating in a moderate-sized beaker covered with a watch-glass. When complete solution has ensued, and the color of the fluid shows that all the iron is dissolved as sesquioxide (if this is not the case some more nitric acid must be added), rinse the watch-glass, dilute the fluid to about 150 c. c., heat to incipient ebullition, add ammonia in moderate excess, filter through a filter exhausted with hydrochloric acid, &c. (Comp. § 113, 1, *a*.) If BUNSEN's methods are employed, proceed exactly as described on pp. 72, 73, and 77.

As the sesquioxide of iron generally contains a small quantity of silicic acid (partially arising from the silicon in the wire, partially taken up from the glass vessels), after it is weighed, digest with fuming hydrochloric acid for some hours; when the oxide of iron is all dissolved, dilute, collect the silica on a small filter, ignite and weigh. The weight is the silica + the ashes of both filters.

The records are made as follows:—

Watch-glass + iron	10·3192
" empty	9·9750
Iron	·3442
Crucible + sesquioxide of iron + silica + filter ash	17·0703
" empty	16·5761
	·4942
Ash of large filter	·0008
Sesquioxide of iron + silica	·4934
Crucible + silica + ashes of both filters	16·5809
" empty	16·5761
	·0048
Ashes of the filters	·0014
Silica	·0034

·4934 — ·0034 = ·4900 sesquioxide of iron = ·343 iron which gives 99·65 per cent.

3. ACETATE OF LEAD.

Determination of Oxide of Lead.—Triturate the dry and non-effloresced crystals* in a porcelain mortar, and press the powder between sheets of blotting paper until fresh sheets are no longer moistened by it.

a. Weigh about 1 grm., dissolve in water with addition of a few drops of acetic acid, and proceed exactly as directed § 116, 1, *a.*

b. Weigh about 1 grm., and proceed exactly as directed § 116, 3.

PbO	111·54	58·84
$\bar{A}$	51·00	26·91
3 aq.	27·00	14·25
	189·54	100·00

4. POTASH ALUM.

Determination of Alumina.—Press pure triturated potash alum between sheets of blotting paper; weigh off about 2 grm., dissolve in water, and determine the alumina as directed § 105, *a.*

KO	47·11	9·93
Al_2O_3	51·36	10·82
4 SO_3	160·00	33·72
24 HO	216·00	45·53
	474·47	100·00

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* Obtained by dissolving the pulverized commercial salt in hot water to saturation, filtering, adding a drop or two of acetic acid to the solution, and slowly evaporating to crystallization.

5. BICHROMATE OF POTASH.

Determination of Chromium.—Fuse pure bichromate of potash at a gentle heat, weigh off ·4—·6 grm., dissolve in water, reduce with hydrochloric acid and spirit of wine, and proceed as directed § 130, I., *a*, *α*.

KO..................	47·11	31·92
2 CrO_3..............	100·48	68·08
	147·59	100·00

6. ARSENIOUS ACID.

Dissolve about 0·2 grm. pure arsenious acid in small lumps in a middle-sized flask, with a glass stopper, in some solution of soda, by digesting on the water-bath; dilute with a little water, add hydrochloric acid in excess, and then nearly fill the flask with clear sulphuretted hydrogen water. Insert the stopper and shake. If the sulphuretted hydrogen is present in excess, the precipitation is terminated; if not, conduct an excess of sulphuretted hydrogen gas into the fluid; proceed in all other respects exactly as directed § 127, 4.

As......................	75	75·76
O_3......................	24	24·24
	99	100·00

B. COMPLETE ANALYSIS OF SALTS IN THE GRAVIMETRIC WAY; CALCULATION OF THE FORMULÆ FROM THE RESULTS OBTAINED. (§§ 202, 203.)

7. CARBONATE OF LIME.

Heat pure carbonate of lime in powder (no matter whether Iceland spar or the artificially prepared substance, see "Qual. Anal.," Am. Ed., p. 83) gently in a platinum crucible.

a. *Determination of Lime.*—Dissolve in a covered beaker, about 1 grm. in dilute hydrochloric acid, heat gently until the carbonic acid is completely expelled, and determine the lime as directed § 103, 2, *b*, *α*.

b. *Determination of Carbonic Acid.*—Determine in about 0·8 grm. the carbonic acid after § 139, II., *d*, *cc*.

CaO....................	28	56·00
CO_2....................	22	44·00
	50	100·00

8. SULPHATE OF COPPER.

Triturate the pure crystals * in a porcelain mortar, and press the powder between sheets of blotting paper.

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* [Boil a solution of commercial blue vitriol with a little pure binoxide of lead (see "Qual. Anal.," Am. Ed., p. 58), to sesquioxidize the iron, then with a little carbonate of baryta, to precipitate it, filter and crystallize. H. WURTZ, Am. Jour. (2), XXVI. 367.]

a. Determination of Water of Crystallization.—1. Weigh off in a crucible 1—2 grm. of the salt, and, having first heated the air-bath (Fig. 22, p. 39) so that the thermometer stands steadily at 120°—140°, introduce the crucible, uncovered, and maintain the heat for two hours. Then cool the crucible in a desiccator and weigh. Heat again as before, for an hour, and weigh. If need be, repeat the heating until no more loss occurs. The loss expresses the amount of water expelled at the temperature of 140°, or four equivalents. 2. Raise the temperature of the air-bath to between 250°—260° and proceed as before. The loss is the one equivalent of strongly combined water of crystallization, or, as some term it, *water of halhydration.*

b. Determination of Sulphuric Acid.—In another portion of the sulphate of copper (about 1·5 grm.) determine the sulphuric acid according to § 132, I., 1.

d. Determination of Oxide of Copper.—In about 1·5 grm. determine the oxide of copper as directed § 119, 1, *a*, *α*.

CuO	39·70	31·83
SO_3	40·00	32·08
HO	9·00	7·22
4 aq	36·00	28·87
	124·70	100·00

9. CRYSTALLIZED PHOSPHATE OF SODA.

a. Determination of the Water of Crystallization.—Heat about 1 grm. of the pure uneffloresced salt in a platinum crucible, slowly and moderately, first in the water-bath, then in the air-bath, and finally some distance above the lamp (not to visible redness); the loss of weight gives the amount of water of crystallization.

b. Determination of the Water of Constitution.—Ignite the residue of *a*.

c. Determination of Phosphoric Acid.

α. Treat 1·5—2 grm. of the salt as directed § 134, *b*, *α*.

β. Treat about 1 grm. of the salt after § 134, *c*.

γ. Treat about 0·2 grm. of the salt as directed § 134, *b*, *β*.

I recommend the student to perform the determination by each of these methods, as they are all in common use in the analytical laboratory.

d. Determination of Soda.—Treat about 1·5 grm. of the salt according to § 135, *a*, *α*. After the excess of lead has been separated with hydrosulphuric acid, the fluid is to be evaporated to dryness and weighed in a platinum dish; comp. § 69, *b*, and § 98, 2.

PO_5	71·00	19·83
$2NaO$	62·00	17·32
HO	9·00	2·51
24 aq	216·00	60·34
	358·00	100·00

10. CHLORIDE OF SILVER.

Ignite pure fused chloride of silver in a stream of pure dry hydrogen till complete decomposition is effected, and weigh the silver obtained. The ignition may be performed in a light bulb tube, or in a porcelain boat in a glass tube, or in a porcelain crucible with perforated cover (§ 115, 4).

The chlorine may be in this case estimated by difference; if you want to determine it directly, proceed as directed § 141, II., *b*.

Ag..................	107·97	75·28
Cl..................	35·46	24·72
	143·43	100·00

11. SULPHIDE OF MERCURY.

Reduce to a fine powder, and dry at 100°.

a. Determination of Sulphur.—Treat about 0·5 grm., as directed § 148, *β*, p. 326, using nitric acid and chlorate of potassa. Precipitate with chloride of barium, and after decanting the clear liquid into a filter, boil the sulphate of baryta twice with dilute solution of acetate of ammonia, and finally wash with hot water.

b. Determination of Mercury.—Dissolve about 0·5 grm. as before, dilute, and allow to stand in a moderately warm place until the smell of chlorine has nearly gone off; filter if necessary, add ammonia in excess, heat gently for some time, add hydrochloric acid until the white precipitate of chloride of mercury and amide of mercury is redissolved, and treat the solution, which now no longer smells of chlorine, as directed § 118, 3.

Hg..................	100.00	86·21
S....................	16·00	13·79
	116·00	100·00

12. CRYSTALLIZED SULPHATE OF LIME.

Select clean and pure crystals of selenite, triturate, and dry under the desiccator (§ 27).

a. Determination of Water.—After § 35, *a*, *α*.

b. Determination of Sulphuric Acid and Lime (§ 132, II., *b*, *α*).

CaO.....................	28	32·56
SO_3.....................	40	46·51
2 aq.....................	18	20·93
	86	100·00

C. SEPARATION OF TWO BASES OR TWO ACIDS FROM EACH OTHER, AND DETERMINATIONS IN THE VOLUMETRIC WAY.

13. SEPARATION OF IRON FROM MANGANESE.

Dissolve in hydrochloric acid about 0·2 grm. fine pianoforte wire, and about the same quantity of ignited protosesquioxide of manganese (prepared as directed § 109, 1 a); heat with a little nitric acid, and separate the two metals by means of acetate of soda (p. 363, 70). Determine the manganese as directed § 109, 3.

14. VOLUMETRIC DETERMINATION OF IRON BY SOLUTION OF PERMANGANATE OF POTASSA.

a. Graduation of the Solution of Permanganate of Potassa.

α. By metallic iron (fine piano wire). 0·2 grm. to be dissolved in dilute sulphuric acid (p. 194). Use the iron wire, a portion of which has been analyzed in Exercise 2, and correct for impurities accordingly.

β. By oxalate of ammonia. 0·2—0·3 grm. to be weighed off (p. 196).

b. Determination of the Protoxide of Iron in double Sulphate of Protoxide of Iron and Ammonia.

α. In solution acidified with sulphuric acid (p. 197, *β*).

β. In solution acidified with hydrochloric acid (p. 198, note).

The formula requires 18·37 per cent. of $Fe\,O$.

c. Determination of the Iron in a Limonite.

Powder finely, dry at 100°, weigh off 2 grm., heat with strong hydrochloric acid till the sesquioxide of iron is completely dissolved, dilute, filter, make the solution up to 200 c.c., and mix. In 20 c.c. of this solution determine the iron after § 113, 3, *a*, p. 203. Reserve half of the solution for the next exercise (see also p. 524).

15. VOLUMETRIC DETERMINATION OF IRON WITH HYPOSULPHITE OF SODA.

a. Graduation of the Solution of Hyposulphite of Soda.

α. By solution of sesquichloride of iron (p. 204).

β. By ammonia-iron-alum (p. 204).

b. Determination of Iron in Limonite.

Use 20 c. c. of the solution obtained in Exercise 14, c., after making sure that the iron all exists in the state of sesquioxide (see p. 192, 1, *a*.)

16. DETERMINATION OF NITRIC ACID IN NITRATE OF POTASSA.

Heat pure nitre, not to fusion, and transfer it to a tube provided with a cork.

a. Treat 0·5 grm. as directed p. 329, *β*.

b. In 0·2 to 0·3 grm., estimate nitric acid according to p. 330, *d*, *α*.

$K\,O$	47·11	46·59
$N\,O_5$	54·00	53·41
	101·11	100·00

17. SEPARATION OF MAGNESIA FROM SODA.

Dissolve about 0·4 grm. pure recently ignited magnesia* and about 0·5 grm. pure well-dried chloride of sodium in dilute hydrochloric acid

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* This may be prepared according to **19**, p. 345.

(avoiding a large excess), and separate with oxalic acid, after p. 345, **16.**

18. SEPARATION OF POTASH FROM SODA.

Triturate crystallized tartrate of potassa and soda (Rochelle salt), press between blotting paper, weigh off about 1·5 grm., heat in a platinum crucible, gently at first, then for some time to gentle ignition. The carbonaceous residue is first extracted with water, finally with dilute hydrochloric acid, the acid fluid is evaporated in a weighed platinum dish, and the chlorides are weighed together (§ 97, 3). Then separate them by bichloride of platinum (p. 339, **1**), and calculate from the results the quantities of soda and potassa severally contained in the Rochelle salt.

KO	47·11	16·70
NaO	31·00	10·99
$C_8H_4O_{10}$	132·00	46·79
8 aq.	72·00	25·52
	282·11	100·00

19. VOLUMETRIC DETERMINATION OF CHLORINE IN CHLORIDES.

a. Preparation and examination of the solution of nitrate of silver (§ 141. I., *b.* *a*).

b. Indirect determination of the soda and potassa in Rochelle salt, by volumetric estimation of the chlorine in the alkaline chlorides prepared as in No. 18. For calculation, see § 197, *a* (p. 465).

20. SEPARATION OF ZINC FROM CADMIUM.

Dissolve in hydrochloric acid about 0·4 grm. of pure oxide of cadmium, and about the same quantity of pure oxide of zinc, both recently ignited, and separate the metals as directed p. 376, **95.**

21. ACIDIMETRY.

a. Preparation of standard sulphuric acid and solution of soda. (§ 204, *a.*) pp. 490–493.

b. Determination of acid in hydrochloric acid, by the specific gravity (p. 487).

c. Determination of acid in the same hydrochloric acid, by an alkaline fluid of known strength (p. 494).

d. Determination of acid in colored vinegar, by saturation with a standard alkaline solution. (Application of test papers, p. 496. *β.*)

e. Preparation of an ammoniacal solution of sulphate of copper (§ 205); determination of its strength by normal sulphuric acid; estimation of the acid in the hydrochloric acid used in *c* and *d*, by means of the copper solution; in this latter process the student may also add to the hydrochloric acid some neutral sulphate of zinc.

22. ALKALIMETRY.

a. Preparation of the test acid after DESCROIZILLES and GAY-LUSSAC (§ 207).

b. Valuation of a soda-ash after expulsion of the water by gentle ignition.

α. After Descroizilles and Gay-Lussac (p. 499).
β. After Mohr (p. 500).

23. Determination of Ammonia.

Treat about 0·8 grm. chloride of ammonium as directed § 99, 3, *a.*

NH_4Cl..	18·00...	33·67	NH_3....	17·00...	31·80
Cl......	35·46...	66·33	HCl....	36·46...	68·20
	53·46	100·00		53·46	100·00

24. Separation of Iodine from Chlorine.

Dissolve about 0·5 grm. pure iodide of potassium and about 2—3 grm. pure chloride of sodium to 250 c. c., and determine the iodine and chlorine:—

a. In 50 c. c., after § 169, 2, *a* (**203**). Calculation § **198**, c.
b. In 50 c. c., after § 169, 2, *b* (**204**).
c. In 10 c. c., after § 169, 2, *c* (**205**).

D. ANALYSIS OF ALLOYS, MINERALS, INDUSTRIAL PRODUCTS, ETC., IN THE GRAVIMETRIC AND VOLUMETRIC WAY.

25. Analysis of Brass.

Brass consists of from 25 to 35 per cent. of zinc and from 75 to 65 per cent. of copper. It also contains usually small quantities of tin and lead, and occasionally traces of iron.

Dissolve about 20 grm. in nitric acid, evaporate on the water-bath to dryness, moisten the residue with nitric acid, add some water, warm, dilute still further, and filter off any residual binoxide of tin (§ 126, 1, *a*). Add to the filtrate, or, if the quantity of tin is very inconsiderable, directly to the solution, about 20 c. c. dilute sulphuric acid; evaporate to dryness on the water-bath, add 50 c. c. water, and apply heat. If a residue remains (sulphate of lead), filter it off, and treat it as directed § 116, 3. In the filtrate, separate the copper from the zinc by hyposulphite of soda (p. 377, **99**). If the quantity of iron present can be determined, determine it in the weighed oxide of zinc (§ 160).

26. Analysis of Solder (Tin and Lead).

Introduce about 1·5 grm. of the alloy, cut into small pieces, into a flask, treat it with nitric acid, and proceed as directed p. 391, **133**, to effect the separation and estimation of the tin.

Mix the filtrate in a porcelain dish with pure dilute sulphuric acid, evaporate the nitric acid on the water bath, and proceed with the sulphate of lead obtained as directed § 116, 3. Test the fluid filtered from the sulphate of lead with sulphuretted hydrogen and sulphide of ammonium for the other metals which the alloy might contain besides tin and lead. The binoxide of tin may contain small quantities of iron or copper; it is tested for these by fusion with carbonate of soda and sulphur (p. 389, *β*).

27. Analysis of a Dolomite.

See § 221.

28. Analysis of Felspar.

a. Decomposition by carbonate of soda (§ 140, II., *b.*); removal of the silicic acid; precipitation of the alumina together with the small quantity of sesquioxide of iron by ammonia (in platinum or Berlin porcelain, not in glass vessels) after § 161, 3 (**88**); separation of baryta, if present, from the filtrate with dilute sulphuric acid, and then of lime with oxalate of ammonia, § 154 (**23**). Finally, separation of the alumina from the sesquioxide of iron generally present in small quantity (§ 160).

b. Decomposition by Smith's method, p. 303. Separate the alkalies after § 152, **1**.

c. Determined loss by ignition.

29. Assay of a Calamine or Smithsonite.

After § 228.
Volumetric determination of the zinc.

30. Analysis of Galena.

a. Determination of the sulphur, lead, iron, &c., as directed § 225.
b. Determination of the silver after § 226.

31. Valuation of Chloride of Lime (§ 211).

a. After Penot (p. 505).

b. After Bunsen (p. 508).—The solutions to be prepared and the separated iodine to be determined as directed § 146 (p. 314).

32. Valuation of Manganese (§ 214).

a. After Fresenius and Will (p. 509).
b. After Bunsen (p. 512).
c. By means of iron (p. 512).

33. Analysis of Gunpowder.

After (p. 514).

E. DETERMINATION OF THE SOLUBILITY OF SALTS.

34. Determination of the Degree of Solubility of Common Salt.

a. At boiling heat.—Dissolve perfectly pure pulverized chloride of sodium in distilled water, in a flask, heat to boiling, and keep in ebullition until part of the dissolved salt separates. Filter the fluid now with the greatest expedition, through a funnel surrounded with boiling water and covered with a glass plate, into an accurately tared capacious measuring flask. As soon as about 100 c. c. of fluid have passed into the flask, insert the cork, allow to cool, and weigh. Fill the flask now up to the mark with water, and determine the salt in an aliquot portion of the fluid, by evaporating in a platinum dish (best with addition of some chloride of ammonium, which will, in some measure, prevent decrepitation); or by determining the chlorine (§ 141).

b. At 14°.—Allow the boiling saturated solution to cool down to this temperature with frequent shaking, and then proceed as in *a*.

100 parts of water dissolve at 109·7° .... 40·35 of chloride of sodium.
100 " " 14° .... 35·87 " "

35. Determination of the Degree of Solubility of Sulphate of Lime.

a. At 100°.
b. At 12°.

Digest pure pulverized sulphate of lime for some time with water, in the last stage of the process at 40—50° (at which temperature sulphate of lime is most soluble); shake the mixture frequently during the process. Decant the clear solution, together with a little of the precipitate, into two flasks, and boil the fluid in one of them for some time; allow that in the other to cool down to 12°, with frequent shaking, and let it stand for some time at that temperature. Then filter both solutions, weigh the filtrates, and determine the amount of sulphate of lime respectively contained in them, by evaporating and igniting the residues.

100 parts of water dissolve at 100° .... 0·217 of anhydrous sulphate of lime.
100 " " 12° .... 0·233 " "

F. DETERMINATION OF THE SOLUBILITY OF GASES IN FLUIDS, AND ANALYSIS OF GASEOUS MIXTURES.

36. Determination of the Absorption-Coefficient of Sulphurous Acid.

See Annal. d. Chem. u. Pharm., vol. 95, page 1; also § 131, 2.

37. Analysis of Atmospheric Air.

See §§ 240—242.

G. ORGANIC ANALYSIS AND DETERMINATIONS OF THE EQUIVALENTS OF ORGANIC BODIES; ALSO ANALYSES IN WHICH ORGANIC ANALYSIS IS APPLIED.

38. Analysis of Tartaric Acid.

Select clean and white crystals. Powder and dry at 100°.

a. Burn with oxide of copper (§§ 174—175).

b. Burn with oxide of copper and finish with oxygen gas (§ 176).
c. Burn in oxygen (§ 178).

C_8	48	32
H_6	6	4
O_{12}	96	64
	150	100

39. DETERMINATION OF THE NITROGEN IN CRYSTALLIZED FERROCYANIDE OF POTASSIUM.

Triturate the perfectly pure crystals, dry the powder in the desiccator (§ 27), and determine the nitrogen as directed § 185. The formula requires 19·87 per cent. of nitrogen.

40. ANALYSIS OF URIC ACID (or any other perfectly pure organic compound of carbon, hydrogen, oxygen, and nitrogen).

Dry pure uric acid at 100°.
a. Determination of the carbon and hydrogen (§ 183).
b. Determination of the nitrogen.
  α. After § 185.
  β. After DUMAS (§ 184).

C_5	30	35·71
N_2	28	33·33
H_2	2	2·38
O_3	24	28·58
	84	100·00

41. ANALYSIS OF A SUPERPHOSPHATE (§ 235).

42. ANALYSIS OF COAL (§ 239).

43. ANALYSIS OF ETHER.

The portion employed must have been rendered anhydrous by digestion with fused chloride of calcium and recently rectified.
Process § 180.

C_8	48	64·87
H_{10}	10	13·51
O_2	16	21·62
	74	100·00

44. ANALYSIS AND DETERMINATION OF THE EQUIVALENT OF BENZOIC ACID.

a. Determination of the silver in benzoate of silver as directed § 115, 1 or 4.

b. Determination by any suitable method of the carbon and hydrogen in the hydrated acid dried at 100°. Calculation, § 200.

45. ANALYSIS AND DETERMINATION OF THE EQUIVALENT OF AN ORGANIC BASE.

Analysis of the base and its double salt with platinum. Calculation, § 200.

46. DETERMINATION OF THE DENSITY OF CAMPHOR VAPOR.

Method described § 191. Calculation, 201.

47. ANALYSIS OF A CAST IRON.

After § 230.

APPENDIX.

ANALYTICAL EXPERIMENTS.*

1. ACTION OF WATER UPON GLASS AND PORCELAIN VESSELS, IN THE PROCESS OF EVAPORATION (to § 41).

A large bottle was filled with water cautiously distilled from a copper boiler with a tin condensing tube. All the experiments in 1 were made with this water.

a. 300 c. c., cautiously evaporated in a platinum dish, left a residue weighing, after ignition, 0·0005 grm. = 0·0017 per 1000.

b. 600 c. c. were evaporated, boiling, nearly to dryness, in a wide flask of Bohemian glass; the residue was transferred to a platinum dish, and the flask rinsed with 100 c. c. distilled water, which was added to the residue in the dish; the fluid in the latter was then evaporated to dryness, and the residue ignited.

The residue weighed	0·0104	grm.
Deducting from this the quantity of fixed matter originally contained in the distilled water, viz.	0·0012	"
There remains substance taken up from the glass	0·0092	"

= 0·0153 per 1000.

In three other experiments, made in the same manner, 300 c. c. left, in two 0·0049 grm., in the third 0·0037 grm.; which, calculated for 600 c. c., gives an

average of	0·0090	grm.
And after a deduction of	0·0012	"
	0·0078	"

= 0·013 per 1000.

We may therefore assume that 1 litre of water dissolves, when boiled down to a small bulk in glass vessels, about 14 milligrammes of the constituents of the glass.

c. 600 c. c. were evaporated nearly to dryness in a dish of Berlin porcelain, and in all other respects treated as in *b.*

The residue weighed	0·0015	grm.
Deducting from this the quantity of fixed matter contained in the distilled water, viz.	0·0012	"
There remains substance taken up from the porcelain	0·0003	"

= 0·0005 per 1000.

2. ACTION OF HYDROCHLORIC ACID UPON GLASS AND PORCELAIN VESSELS, IN THE PROCESS OF EVAPORATION (to § 41).

The distilled water used in 1 was mixed with $\frac{1}{10}$ of pure hydrochloric acid.

a. 300 grm., evaporated in a platinum dish, left 0·002 grm. residue.

b. 300 grm., evaporated first in Bohemian glass nearly to dryness, then in a platinum dish, left 0·0019 residue; the dilute hydrochloric acid, therefore, had not attacked the glass.

c. 300 grm. evaporated in Berlin porcelain, &c., left 0·0036 grm., accordingly after deducting 0·002, 0·0016 = 0·0053 per 1000.

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[*] The experiments are numbered as in the original edition, but some are omitted.

d. In a second experiment made in the same manner as in *a.*, the residue amounted to 0·0034, accordingly after deducting 0·002, 0·0014=0·0047 per 1000.

Hydrochloric acid, therefore, attacks glass much less than water, whilst porcelain is about equally affected by water and dilute hydrochloric acid. This shows that the action of water upon glass consists in the formation of soluble basic silicates.

3. ACTION OF SOLUTION OF CHLORIDE OF AMMONIUM UPON GLASS AND PORCELAIN VESSELS, IN THE PROCESS OF EVAPORATION (to § 41).

In the distilled water of 1, $\frac{1}{10}$ of chloride of ammonium was dissolved, and the solution filtered.

a. 300 c. c. evaporated in a platinum dish, left 0·006 grm. fixed residue.

b. 300 c. c., evaporated first nearly to dryness in Bohemian glass, then to dryness in a platinum dish, left 0·0179 grm.; deducting from this 0·006 grm., there remains substance taken up from the glass, 0·0119=0·0397 per 1000.

c. 300 c. c., treated in the same manner in Berlin porcelain, left 0·0178; deducting from this 0·006, there remains 0·0118=0·0393 per 1000.

Solution of chloride of ammonium, therefore, strongly attacks both glass and porcelain in the process of evaporation.

4. ACTION OF SOLUTION OF CARBONATE OF SODA UPON GLASS AND PORCELAIN VESSELS (to § 41).

In the distilled water of 1, $\frac{1}{10}$ of pure crystallized carbonate of soda was dissolved.

a. 300 c. c., supersaturated with hydrochloric acid and evaporated to dryness in a platinum dish, &c., gave 0·0026 grm. silicic acid=0·0087 per 1000.

b. 300 c. c. were gently boiled for three hours in a glass vessel, the evaporating water being replaced from time to time; the tolerably concentrated liquid was then treated as in *a*; it left a residue weighing 0·1876 grm.; deducting from this the 0·0026 grm., left in *a*, there remains 0·185 grm.=0·450 per 1000.

c. 300 c. c., treated in the same manner as in *b*, in a porcelain vessel, left 0·0099; deducting from this 0·0026 grm., there remains 0·0073=0·0243 per 1000.

Which shows that boiling solution of carbonate of soda attacks glass very strongly, and porcelain also in a very marked manner.

5. WATER DISTILLED FROM GLASS VESSELS (to § 56, 1).

42·41 grm. of water distilled with extreme caution from a tall flask with a LIEBIG'S condenser, left upon evaporation in a platinum dish, a residue weighing, after ignition, 0·0018 grm., consequently $\frac{1}{23561}$.

6. SULPHATE OF POTASH AND ALCOHOL (to § 68, *a*).

a. Ignited pure sulphate of potassa was digested cold with absolute alcohol, for several days, with frequent shaking; the fluid was filtered off, the filtrate diluted with water, and then mixed with chloride of barium. It remained perfectly clear upon the addition of this reagent, but after the lapse of a considerable time it began to exhibit a slight opalescence. Upon evaporation to dryness, there remained a very trifling residue, which gave, however, distinct indications of the presence of sulphuric acid.

b. The same salt treated in the same manner, with addition of some pure concentrated sulphuric acid, gave a filtrate which, upon evaporation in a platinum dish, left a clearly perceptible fixed residue of sulphate of potassa.

7. DEPORTMENT OF CHLORIDE OF POTASSIUM IN THE AIR AND AT A HIGH TEMPERATURE (to § 68, *b*).

0·9727 grm. of ignited (not fused) pure chloride of potassium, heated for 10 minutes to dull redness in an open platinum dish, lost 0·0007 grm.; the salt was then kept for 10 minutes longer at the same temperature, when no further diminution of weight was observed. Heated to bright redness and semi-fusion, the salt suffered a further loss of weight to the extent of 0·0009 grm. Ignited intensely and to perfect fusion, it lost 0·0034 grm., more.

Eighteen hours' exposure to the air produced not the slightest increase of weight.

8. SOLUBILITY OF POTASSIO-BICHLORIDE OF PLATINUM IN ALCOHOL (to § 68, *c*).

a. In absence of free Hydrochloric Acid.

α. An excess of perfectly pure, recently precipitated potassio-bichloride of platinum was digested for 6 days at 15—20°, with alcohol of 97·5 per cent., in a stoppered bottle, with frequent shaking. 72·5 grm. of the perfectly colorless filtrate left upon evaporation in a platinum dish, a residue which, dried at 100°, weighed 0·006 grm.; 1 part of the salt requires therefore 12083 parts of alcohol of 97·5 per cent. for solution.

β. The same experiment was made with spirit of wine of 76 per cent. The filtrate might be said to be colorless; upon evaporation, slight blackening ensued, on which account the residue was determined as platinum. 75·5 grm. yielded 0·008 grm. platinum, corresponding to 0·02 grm. of the salt. One part of the salt dissolves accordingly in 3775 parts of spirit of wine of 76 per cent.

γ. The same experiment was made with spirit of wine of 55 per cent. The filtrate was distinctly yellowish. 63·2 grm. left 0·0241 grm. platinum, corresponding to 0·06 grm. of the salt. One part of the salt dissolves accordingly in 1053 parts of spirit of wine of 55 per cent.

b. In presence of free Hydrochloric Acid.

Recently precipitated potassio-bichloride of platinum was digested cold with spirit of wine of 76 per cent., to which some hydrochloric acid had been added. The solution was yellowish; 67 grm. left 0·0146 grm. platinum, which corresponds to 0·0365 grm. of the salt. One part of the salt dissolves accordingly in 1835 parts of spirit of wine, mixed with hydrochloric acid.

9. SULPHATE OF SODA AND ALCOHOL (to § 69, *a*).

Experiments made with pure anhydrous sulphate of soda, in the manner described in 6, showed that this salt comports itself both with pure alcohol, and with alcohol containing sulphuric acid, exactly like the sulphate of potassa.

10. DEPORTMENT OF IGNITED SULPHATE OF SODA IN THE AIR (to § 69, *a*).

2·5169 grm. anhydrous sulphate of soda were exposed, in a watch-glass, to the open air on a hot summer day. The first few minutes passed without any increase of weight, but after the lapse of 5 hours there was an increase of 0·0061 grm.

12. DEPORTMENT OF CHLORIDE OF SODIUM IN THE AIR (to § 69, *b*).

4·3281 grm. of chemically pure, moderately ignited (not fused) chloride of sodium, which had been cooled under a bell-glass over sulphuric acid, acquired during 45 minutes' exposure to the (somewhat moist) air, an increase of weight of 0·0009 grm.

13. DEPORTMENT OF CHLORIDE OF SODIUM UPON IGNITION BY ITSELF AND WITH CHLORIDE OF AMMONIUM (to § 69, *b*).

4·3281 grm. chemically pure, ignited chloride of sodium were dissolved in water, in a moderate-sized platinum dish, and pure chloride of ammonium was added to the solution, which was then evaporated and the residue gently heated until the evolution of chloride of ammonium fumes had apparently ceased. The residue weighed 4·3334 grm. It was then very gently ignited for about 2 minutes, and after this re-weighed, when the weight was found to be 4·3314 grm. A few minutes' ignition at a red heat reduced the weight to 4·3275 grm., and 2 minutes' further ignition at a bright red heat (upon which occasion white fumes were seen to escape), to 4·3249 grm.

14. DEPORTMENT OF CARBONATE OF SODA IN THE AIR AND ON IGNITION (to § 69, *c*).

2·1061 grm. of moderately ignited chemically pure carbonate of soda were exposed to the air in an open platinum dish in July in bad weather; after 10 minutes the weight was 2·1078, after 1 hour 2·1113, after 5 hours [illegible].

1·4212 grm. of moderately ignited chemically pure carbonate of soda were ignited for 5 minutes in a covered platinum crucible; no fusion took place, and the weight was unaltered. Heated more strongly for 5 minutes, it partially fused, and then weighed 1·4202. After being kept fusing for 5 minutes, it weighed 1·4135.

15. DEPORTMENT OF CHLORIDE OF AMMONIUM UPON EVAPORATION AND DRYING (to § 70, *a*).

0·5625 grm. pure and perfectly dry chloride of ammonium was dissolved in water in a platinum dish, evaporated to dryness in the water-bath and completely dried; the weight was now found to be 0·5622 grm. (ratio 100 : 99·94). It was again heated for 15 minutes in the water-bath, and afterwards re-weighed, when the weight was found to be 0·5612 grm. (ratio 100 : 99·77). Exposed once more for 15 minutes to the same temperature, the residue weighed [illegible] grm. (ratio 100 : 99·69).

16. SOLUBILITY OF AMMONIO-BICHLORIDE OF PLATINUM IN ALCOHOL (to § 70, *b*).

a. In absence of free Hydrochloric Acid.

α. An excess of perfectly pure, recently precipitated ammonio-bichloride of platinum was digested for [illegible] days, at [illegible]—20°, with alcohol of 97·5 per cent., in a stoppered bottle, with frequent agitation.

74·3 grm. of the perfectly colourless filtrate left, upon evaporation and ignition in a platinum dish, [illegible] grm. platinum, corresponding to [illegible] of the salt. One part of the salt requires accordingly [illegible] parts of alcohol of 97·5 per cent.

β. The same experiment was made with spirit of wine of 76 per cent. The filtrate was distinctly yellowish.

[illegible] grm. left [illegible] platinum, which corresponds to [illegible] grm. of the salt. One part of the salt dissolves accordingly in 1406 parts of spirit of wine of 76 per cent.

γ. The same experiment was made with spirit of wine of 55 per cent. The filtrate was distinctly yellow. Slight blackening ensued upon evaporation, and 56·5 grm. left [illegible] platinum, which corresponds to [illegible] grm. of the salt. Consequently, 1 part of the salt dissolves in 665 parts of spirit of wine of 55 per cent.

b. In presence of Hydrochloric Acid.

The experiment described in β was repeated, with this modification, that some hydrochloric acid was added to the spirit of wine. [illegible] grm. left [illegible] grm. of platinum, which corresponds to [illegible] grm. of the salt. 672 parts of the acidified spirit had therefore dissolved 1 part of the salt.

17. SOLUBILITY OF CARBONATE OF BARYTA IN WATER (to § [illegible]).

a. In Cold Water.—Perfectly pure, recently precipitated BaO, CO_2 was digested for [illegible] days with water of [illegible]—20°, with frequent shaking. The mixture was filtered, and a portion of the filtrate mixed with sulphuric acid, another portion with ammonia. The former reagent immediately produced turbidity in the fluid, the latter only after the lapse of a considerable time. [illegible] grm. of the solution left, upon evaporation, [illegible] BaO, CO_2. 1 part of that salt dissolves consequently in [illegible] parts of cold water.

b. In Hot Water.—The same carbonate of baryta being boiled for [illegible] minutes with pure distilled water, gave a filtrate manifesting the same reactions as that prepared with cold water, and remaining perfectly clear upon cooling. [illegible] grm. of the hot solution left, upon evaporation, [illegible] grm. of carbonate of baryta. One part of that salt dissolves therefore in [illegible] parts of boiling water.

18. SOLUBILITY OF [illegible] OF BARYTA IN WATER CONTAINING AMMONIA AND CARBONATE OF AMMONIA (to § [illegible]).

A solution of chemically pure chloride of barium was mixed with ammonia and carbonate of ammonia in excess, gently heated and allowed to stand at rest for [illegible] hours; the fluid was then filtered off. The filtrate remained perfectly clear upon addition of sulphuric acid; but after the lapse of a very considerable time, a hardly perceptible precipitate separated. 84·82 grm. of the filtrate left, upon evaporation in a small platinum dish, and subsequent gentle ignition, 0·0006 grm. 1 part of the salt had consequently dissolved in 141000 parts of the fluid.

19. SOLUBILITY OF SILICO-FLUORIDE OF BARIUM IN WATER (to § 71, *c*).

a. Recently precipitated, thoroughly washed silico-fluoride of barium was digested for 4 days in cold water, with frequent shaking; the fluid was then filtered off, and a portion of the filtrate tested with dilute sulphuric acid, another portion with solution of sulphate of lime; both reagents produced turbidity—the former immediately, the latter after one or two seconds—precipitates separated from both portions after the lapse of some time. 84·82 grm. of the filtrate left a residue which, after being thoroughly dried, weighed 0·0223 grm. 1 part of the salt had consequently required 3802 parts of cold water for its solution.

b. A portion of another sample of recently precipitated silico-fluoride of barium was heated with water to boiling, and the solution allowed to cool (upon which a portion of the dissolved salt separated). The cold fluid was left for a considerable time longer in contact with the undissolved salt, and was then filtered off. The filtrate showed the same deportment with solution of sulphate of lime as that of *a*. 84·82 grm. of it left 0·025 grm. One part of the salt had accordingly dissolved in 3392 parts of water.

20. SOLUBILITY OF SILICO-FLUORIDE OF BARIUM IN WATER ACIDIFIED WITH HYDROCHLORIC ACID (to § 71, *c*).

a. Recently precipitated pure silico-fluoride of barium was digested with frequent agitation for 3 weeks with cold water acidified with hydrochloric acid. The filtrate gave with sulphuric acid a rather copious precipitate. 84·82 grm. left 0·1155 grm. of thoroughly dried residue, which, calculated as silico-fluoride of barium, gives 733 parts of fluid to 1 part of that salt.

b. Recently precipitated pure silico-fluoride of barium was mixed with water very slightly acidified with hydrochloric acid, and the mixture heated to boiling. Cooled to 12°, 84·82 grm. of the filtrate left a residue of 0·1322 grm., which gives 640 parts of fluid to 1 part of the salt.

N.B. The solution of silico-fluoride of barium in hydrochloric acid is not effected without decomposition; at least, the residue contained, even after ignition, a rather large proportion of chloride of barium.

21. SOLUBILITY OF SULPHATE OF STRONTIA IN WATER (to § 72, *a*).

a. *In Water* of 14°.

84·82 grm. of a solution prepared by 4 days' digestion of recently precipitated sulphate of strontia with water at the common temperature, left 0·0123 grm. of sulphate of strontia. One part of $Sr\,O, S\,O_3$ dissolves consequently in 6895 parts of water.

b. *In Water* of 100°.

84·82 grm. of a solution prepared by boiling recently precipitated sulphate of strontia several hours with water, left 0·0088 grm. Consequently 1 part of $Sr\,O, S\,O_3$ dissolves in 9638 parts of boiling water.

22. SOLUBILITY OF SULPHATE OF STRONTIA IN WATER CONTAINING HYDROCHLORIC ACID AND SULPHURIC ACID (to § 72, *a*).

a. 84·82 grm. of a solution prepared by 3 days' digestion, left 0·0077 grm. $Sr\,O, S\,O_3$.

b. 42·41 grm. of a solution prepared by 4 days' digestion, left 0·0036 grm.

c. Pure carbonate of strontia was dissolved in an excess of hydrochloric acid, and the solution precipitated with an excess of sulphuric acid and then allowed to stand in the cold for a fortnight. 84·82 grm. of the filtrate left 0·0066 grm.

In *a*.	1 part of $Sr\,O, S\,O_3$ required	11016	parts.
b.	1 " "	11780	"
c.	1 " "	12791	"
	Mean	11862	parts.

23. SOLUBILITY OF SULPHATE OF STRONTIA IN HYDROCHLORIC ACID, AND ACETIC ACID (to § 72, *a*).

a. Recently precipitated pure sulphate of strontia w the cold with nitric acid of 4·8 per cent. 150 grm. of th 1 part of the salt required accordingly 435 parts of the di in another experiment 1 part of the salt was found t dilute acid. Mean, 432 parts.

b. The same salt was digested for 2 days in the cold 8·5 per cent. 100 grm. left 0·2115, and in another ex part of the salt requires, accordingly, in the mean, 4 acid of 8·5 per cent. for its solution.

c. The same salt was digested for 2 days in the col per cent. $\bar{A}, HO$. 100 grm. left 0·0126, and in another 1 part of the salt requires, accordingly, in the mean, 78 15·6 per cent.

24. SOLUBILITY OF CARBONATE OF STRONTIA IN CO

Recently precipitated, thoroughly washed SrO, C days with cold distilled water, with frequent shaking. left, upon evaporation, a residue weighing, after i part of carbonate of strontia requires therefore 1804 solution.

25. SOLUBILITY OF CARBONATE OF STRONTIA AMMONIA AND CARBONATE OF AMMONIA (to § 72, *b*).

Recently precipitated, thoroughly washed carbonate for four weeks with cold water containing ammonia an with frequent shaking. 84·82 grm. of the filtrate left Consequently, 1 part of the salt requires 56545 parts of

If solution of chloride of strontium is precipitated wi and ammonia as directed § 102, 2, *a*, sulphuric acid pr filtrate, after addition of alcohol.

26. SOLUBILITY OF CARBONATE OF LIME IN COLD (to § 73, *b*).

a. A solution prepared by boiling as in 26, *b*, was dig weeks, with frequent agitation, with the undissolved left 0·0080 CaO, CO_2. 1 part therefore required 1060

b. Recently precipitated CaO, CO_2 was boiled for water. 42·41 grm. of the filtrate left, upon evaporati the residue, 0·0048 CaO, CO_2. 1 part requires con boiling water.

27. SOLUBILITY OF CaO, CO_2 IN WATER CONTAININ NATE OF AMMONIA (to § 73, *b*).

Pure dilute solution of chloride of calcium was precip ammonia and ammonia, allowed to stand 24 hours, and left 0·0013 grm. CaO, CO_2. 1 part requires consequen

28. DEPORTMENT OF CARBONATE OF LIME UPON I CRUCIBLE (to § 73, *b*).

0·7955 grm. of perfectly dry carbonate of lime was thin platinum crucible, to the gradually increased, and of a good BERZELIUS' lamp. The crucible was open and the first 15 minutes the mass weighed 0·6482—after half hour 0·5927, which latter weight remained unaltered aft heating. This corresponds to 74·5 per cent., whilst t the carbonate is calculated at 56 per cent.; there rema still a considerable amount of the carbonic acid.

29. COMPOSITION OF OXALATE OF LIME DRIED AT 10

0·8510 grm. of thoroughly dry pure carbonate of lim chloric acid; the solution was precipitated with oxala monia, and the precipitate collected upon a weighed filter and dried at 100°, until the weight remained constant. The oxalate of lime so produced weighed 1·2461 grm. Calculating this as Ca O, $C_2 O_3$+aq., the amount found contained 0·4772 Ca O, which corresponds to 56·07 per cent. in the carbonate of lime; the calculated proportion of lime in the latter is 56 per cent.

30. DEPORTMENT OF SULPHATE OF MAGNESIA IN THE AIR AND UPON IGNITION (to § 74, *a*).

0·8135 grm. of perfectly pure anhydrous Mg O, S O_3 in a covered platinum crucible acquired, on a fine and warm day in June, in half an hour, an increase of weight of 0·004 grm., and in the course of 12 hours, of 0·067 grm. The salt could not be accurately weighed in the open crucible, owing to continual increase of weight.

0·8135 grm., exposed for some time to a very moderate red heat, suffered no diminution of weight; but after 5 minutes' exposure to an intense red heat, the substance was found to have lost 0·0075 grm., and the residue gave no longer a clear solution with water. About 0·2 grm. of pure sulphate of magnesia exposed in a small platinum crucible, for 15 to 20 minutes, to the heat of a powerful blast gaslamp, gave, with dilute hydrochloric acid, a solution in which chloride of barium failed to produce the least turbidity.

31. SOLUBILITY OF THE BASIC PHOSPHATE OF MAGNESIA AND AMMONIA IN PURE WATER (to § 74, *b*).

a. Recently precipitated basic phosphate of magnesia and ammonia was thoroughly washed with water, then digested for 24 hours with water of about 15°, with frequent shaking.

84·42 grm. of the filtrate left................................ 0·0047 grm.
of pyrophosphate of magnesia.

b. The same precipitate was digested in the same manner for 72 hours

84·42 grm. of the filtrate left...................... .... 0·0043 "

Mean 0·0045 "

which corresponds to 0·00552 grm. of the anhydrous double salt. 1 part of that salt dissolves therefore in 15293 parts of pure water.

The cold saturated solution gave, with ammonia, after the lapse of a short time, a distinctly perceptible crystalline precipitate;—on the addition of phosphate of soda, it remained perfectly clear, and even after the lapse of two days no precipitate had formed;—phosphate of soda and ammonia produced a precipitate as large as that by ammonia.

32. SOLUBILITY OF BASIC PHOSPHATE OF MAGNESIA AND AMMONIA IN WATER CONTAINING AMMONIA (to § 74, *b*).

a. Pure basic phosphate of magnesia and ammonia was dissolved in the least possible amount of nitric acid; a large quantity of water was added to the solution, then ammonia in excess. The mixture was allowed to stand at rest for 24 hours, then filtered; its temperature was 14°. 84·42 grm. left 0·0015 pyrophosphate of magnesia, which corresponds to 0·00184 of the anhydrous double salt. Consequently 1 part of the latter requires 45880 parts of ammoniated water for its solution.

b Pure basic phosphate of magnesia and ammonia was digested for 4 weeks with ammoniated water, with frequent shaking; the fluid (temperature 14°) was then filtered off; 126·63 grm. left 0·0024 pyrophosphate of magnesia, which corresponds to 0·00296 of the double salt. 1 part of it therefore dissolves in 42780 parts of ammoniated water. Taking the mean of *a* and *b*, 1 part of the double salt requires 44330 parts of ammoniated water for its solution.

33. ANOTHER EXPERIMENT ON THE SAME SUBJECT (to § 74, *b*).

Recently precipitated phosphate of magnesia and ammonia, most carefully washed with water containing ammonia, was dissolved in water acidified with hydrochloric acid, ammonia added in excess, and allowed to stand in the cold for 24 hours. 169·64 grm. of the filtrate left 0·0031 pyrophosphate of magnesia, corresponding to 0·0038 of anhydrous phosphate of magnesia and ammonia. 1 part of the double salt required therefore 44600 parts of the fluid.

34. SOLUBILITY OF THE BASIC PHOSPHATE OF MAGNESIA AND AMMONIA IN WATER CONTAINING CHLORIDE OF AMMONIUM (to § 74, *b*).

Recently precipitated, thoroughly washed basic phosphate of magnesia and ammonia was digested in the cold with a solution of 1 part of chloride of ammonium in 5 parts of water. 18·4945 grm. of the filtrate left 0·002 pyrophosphate of magnesia, which corresponds to 0·00245 of the double salt. 1 part of the salt dissolves therefore in 7548 parts of the fluid.

35. SOLUBILITY OF THE BASIC PHOSPHATE OF MAGNESIA AND AMMONIA IN WATER CONTAINING AMMONIA AND CHLORIDE OF AMMONIUM (to § 74, *b*).

Recently precipitated, thoroughly washed phosphate of magnesia and ammonia was digested in the cold with a solution of 1 part of chloride of ammonium in 7 parts of ammoniated water. 23·1283 grm. of the filtrate left 0·0012 pyrophosphate of magnesia, which corresponds to 0·00148 of the double salt. 1 part of the double salt requires consequently 15627 parts of the fluid for its solution.

36. DEPORTMENT OF ACID SOLUTIONS OF PYROPHOSPHATE OF MAGNESIA WITH AMMONIA (to § 74, *c*).

0·3985 grm. pyrophosphate of magnesia was treated for several hours, at a high temperature, with concentrated sulphuric acid. This exercised no perceptible action. It was only after the addition of some water that the salt dissolved. The fluid, heated for some time, gave, upon addition of ammonia in excess, a crystalline precipitate, which was filtered off after 18 hours; the quantity of pyrophosphate of magnesia obtained was 0·3805 grm., that is, 95·48 per cent. Phosphate of soda produced in the filtrate a trifling precipitate, which gave 0·0150 grm. of pyrophosphate of magnesia, that is, 3·76 per cent.

0·3565 grm. pyrophosphate of magnesia was dissolved in 3 grm. nitric acid, of 1·2 sp. gr.; the solution was heated, diluted, and precipitated with ammonia: the quantity of pyrophosphate of magnesia obtained amounted to 0·3485 grm., that is, 98·42 per cent.; 0·4975 grm. was treated in the same manner with 7·6 grm. of the same nitric acid: the quantity re-obtained was 0·4935 grm., that is, 99·19 per cent.

0·786 grm. treated in the same manner with 16·2 grm. of nitric acid, gave 0·7765 grm., that is, 98·79 per cent.

The result of these experiments may be tabulated thus:—

Proportion of $2\,MgO.\,PO_5$ to nitric acid.	Re-obtained.	Loss.
1 : 9	98·42 per cent.	1·58
1 : 15	99·19 "	0·81
1 : 20	98·79 "	1·21

37. SOLUBILITY OF PURE MAGNESIA IN WATER (to § 74, *d*).

a. In Cold Water.

Perfectly pure well-crystallized sulphate of magnesia was dissolved in water, and the solution precipitated with carbonate of ammonia and caustic ammonia; the precipitate was thoroughly washed—in spite of which it still retained a perceptible trace of sulphuric acid—then dissolved in pure nitric acid, an excess of acid being carefully avoided. The solution was then re-precipitated with carbonate of ammonia and caustic ammonia, and the precipitate thoroughly washed. The so-prepared perfectly pure basic carbonate of magnesia was ignited in a platinum crucible until the weight remained constant. The residuary pure magnesia was then digested in the cold for 24 hours with distilled water, with frequent shaking. The distilled water used was perfectly free from chlorine, and left no fixed residue upon evaporation.

α. 84·82 grm. of the filtrate, cautiously evaporated in a platinum dish, left a residue weighing, after ignition, 0·0015 grm. 1 part of the pure magnesia dissolved therefore in.. 56546 parts of cold water.

The digestion was continued for 48 hours longer, when

β. 84·82 grm. left 0·0016 grm. 1 part required therefore.......... 53012

γ. 84·82 grm. left 0·0015 grm. 1 part required.................... 56546

Average 55368

The solution of magnesia prepared in the cold way has a feeble yet distinct alkaline reaction, which is most easily perceived upon the addition of very faintly reddened tincture of litmus; the alkaline reaction of the solution is perfectly manifest also with slightly reddened litmus paper, or with turmeric or dahlia paper, if these test-papers are left for some time in contact with the solution.

Alkaline carbonates fail to render the solution turbid, even upon boiling.

Phosphate of soda also fails to impair the clearness of the solution, but if the fluid is mixed with a little ammonia and shaken, it speedily becomes turbid, and deposits after some time a perceptible precipitate of basic phosphate of magnesia and ammonia.

b. In Hot Water.

Upon boiling pure magnesia with water, a solution is obtained which comports itself in every respect like the cold-prepared solution of magnesia. A hot-prepared solution of magnesia does not become turbid upon cooling, nor does a cold-prepared solution upon boiling. 84·82 grm. of hot-prepared solution of magnesia left 0·0016 grm. Mg O.

38. Solubility of Pure Magnesia in Solutions of Chloride of Potassium and Chloride of Sodium (to § 74, *d*).

3 flasks of equal size were charged as follows:—

1. With 1 grm. pure chloride of potassium, 200 c. c. water and some perfectly pure magnesia.
2. With 1 grm. pure chloride of sodium, 200 c. c. water and some pure magnesia.
3. With 200 c. c. water and some pure magnesia.

The contents of the 3 flasks were kept boiling for 40 minutes, then filtered, and the clear filtrates mixed with equal quantities of a mixture of phosphate of soda, chloride of ammonium and ammonia. After 12 hours a very slight precipitation was visible in 3, and a considerably larger precipitation had taken place in 1 and 2.

39. Precipitation of Alumina by Ammonia, etc. (to § 75, *a*).

a. Ammonia produces in neutral solutions of salts of alumina or of alum, as is well known, a gelatinous precipitate of hydrate of alumina. Upon further addition of ammonia in considerable excess, the precipitate redissolves gradually, but not completely.

b. If a drop of a dilute solution of alum is added to a copious amount of ammonia, and the mixture shaken, the solution appears almost perfectly clear; however, after standing at rest for some time, slight flakes separate.

c. If a solution of alumina, mixed with a large amount of ammonia, is filtered, and

α. The filtrate boiled for a considerable time, flakes of hydrate of alumina separate gradually in proportion as the excess of ammonia escapes.

β. The filtrate mixed with solution of chloride of ammonium, a very perceptible flocculent precipitate of hydrate of alumina separates immediately; the whole of the hydrated alumina present in the solution will thus separate if the chloride of ammonium be added in sufficient quantity.

γ. The filtrate mixed with sesquicarbonate of ammonia, the same reaction takes place as in *β*.

δ. The filtrate mixed with solution of chloride of sodium or chloride of potassium, no precipitate separates, but, after several days' standing, slight flakes of hydrate of alumina subside, owing to the loss of ammonia by evaporation.

d. If a neutral solution of alumina is precipitated with carbonate of ammonia, or if a solution strongly acidified with hydrochloric or nitric acid is precipitated with pure ammonia, or if to a neutral solution a sufficient amount of chloride of ammonium is added besides the ammonia; even a considerable excess of the precipitants will fail to redissolve the precipitated alumina, as appears from the continued perfect clearness of the filtrates upon protracted boiling and evaporation.

40. Precipitation of Alumina by Sulphide of Ammonium (to § 75, *a*).

(*Experiments made by Mr.* J. Fuchs, *formerly Assistant in my Laboratory.*)

a. 50 c. c. of a solution of pure ammonia-alum, which contained 0·3939 [illegible] c. c. water and 10 c. c. solution of sulphide of [illegible] ten minutes. The ignited precipitate weighed [illegible]

[illegible] was repeated with 100 c. c. water; the precipitate [illegible]

[illegible] was repeated with 200 c. c. water; the precipitate [illegible]

[illegible] SESQUIOXIDE OF CHROMIUM BY AMMONIA (to §

[illegible]le of chromium and of chrome-alum (concentrated [illegible] acidified with hydrochloric acid) were mixed with am- [illegible] the filtrates drawn off immediately after precipitation ap- [illegible] filtered after ebullition, they all appeared colorless, if the [illegible] sufficiently protracted.

[illegible] THE BASIC CARBONATE OF ZINC IN WATER (to § 77, *a*).

[illegible] recently (hot) precipitated basic carbonate of zinc was gently [illegible] distilled water, and subsequently digested cold for many weeks, [illegible]. The clear solution gave no precipitate with sulphide of [illegible] even after long standing.

[illegible] 0·0014 grm. oxide of zinc, which corresponds to 0·0019 [illegible] of zinc (74 per cent. of Zn O being assumed in this salt). [illegible] the basic carbonate requires therefore 44642 parts of water for so- [illegible]

[illegible] THE THREE FOLLOWING NUMBERS THE SULPHIDE WAS PRE- [illegible] the solution of the neutral salt with addition of chloride of ammo- [illegible] sulphide of ammonium, and allowed to stand in a closed vessel. [illegible] the clear fluid was poured on to 6 filters of equal size, and the [illegible] then equally distributed among them. The washing was at [illegible] and continued, without interruption, the following fluids being [illegible]

[illegible] water.
[illegible] containing sulphuretted hydrogen.
[illegible] containing sulphide of ammonium.
[illegible] containing chloride of ammonium, afterwards pure water.
[illegible] containing sulphuretted hydrogen and chloride of ammonium, afterwards water containing sulphuretted hydrogen.
[illegible] containing sulphide of ammonium and chloride of ammonium, afterwards water containing sulphide of ammonium.

[illegible]MENT OF SULPHIDE OF ZINC ON WASHING (to § 77, *c*).

[illegible] were at first colorless and clear. On washing, the first three fil- [illegible] through turbid, the turbidity was strongest in II. and weakest in [illegible] three remained quite clear. On adding sulphide of ammonium no [illegible]; the turbidity of the first three was not increased, the clear- [illegible] three was not impaired. Chloride of ammonium therefore de- [illegible] favorable action, and the water containing it may be displaced [illegible] sulphide of ammonium.

[illegible]MENT OF SULPHIDE OF MANGANESE ON WASHING (to § 78, *e*).

[illegible] were at first clear and colorless. But after the washing had [illegible] some time, I. appeared colorless, slightly opalescent; II. [illegible] turbid; III. yellowish and turbid; IV. colorless, slightly turbid; [illegible] yellowish, nearly clear; VI. clear, yellowish. To obtain a filtrate [illegible] clear, therefore, the wash-water must at first contain chloride of [illegible] Addition of sulphide of ammonium also cannot be dispensed [illegible] the filtrates obtained without this addition gave distinct pre- [illegible] sulphide of manganese when the reagent was subsequently added to [illegible]

45. Deportment of Sulphide of Nickel (also of Sulphide of Cobalt and Sulphide of Iron) on Washing (to § 79, *d*).

In the experiments with sulphide of nickel the clear filtrates were put aside, and then the washing was proceeded with. The washings of the first 3 ran through turbid, of the last 3 clear. When the washing was finished, I. was colorless and clear; II. blackish and clear; III. dirty yellow and clear; IV. colorless and clear; V. slightly opalescent; VI. slightly brownish and opalescent. On addition of sulphide of ammonium, I. became brown; II. remained unaltered; III. remained unaltered; IV. became black and opaque; V. became brown and clear; VI. became pure yellow and clear.

Sulphide of cobalt and sulphide of iron behaved in an exactly similar manner. It is plain that these sulphides oxidize more rapidly when the wash-water contains chloride of ammonium, unless sulphide of ammonium is also present. Hence it is necessary to wash with a fluid containing sulphide of ammonium; and the addition of chloride of ammonium at first is much to be recommended, as this diminishes the likelihood of our obtaining a muddy filtrate.

46. Deportment of Hydrate of Protoxide of Cobalt precipitated by Alkalies (to § 80, *a*).

A solution of protochloride of cobalt was precipitated boiling with solution of soda, and the precipitate washed with boiling water until the filtrate gave no longer the least indication of presence of chlorine. The dried and ignited residue, heated with water, manifested no alkaline reaction. It was reduced by ignition in hydrogen gas, and the metallic cobalt digested hot with water. The decanted water manifested no alkaline reaction, even after considerable concentration; but the metallic cobalt, brought into contact, moist, with turmeric paper, imparted to the latter a strong brown color.

47. Solubility of Carbonate of Lead (to § 83, *a*).

a. In pure Water.

Recently precipitated and thoroughly washed pure carbonate of lead was digested for 8 days with water at the common temperature, with frequent shaking. 84·42 grm. of the filtrate were evaporated, with addition of some pure sulphuric acid; the residuary sulphate of lead weighed 0·0019 grm., which corresponds to 0·00167 carbonate of lead. One part of the latter salt dissolves therefore in 50551 parts of water. The solution, mixed with sulphuretted hydrogen water, remained perfectly colorless, not the least tint being detected in it, even upon looking through it from the top of the test-cylinder.

b. In Water containing a little Acetate of Ammonia and also Carbonate of Ammonia and Ammonia.

A highly dilute solution of pure acetate of lead was mixed with carbonate of ammonia and ammonia in excess, and the mixture gently heated and then allowed to stand at rest for several days. 84·42 grm. of the filtrate left, upon evaporation with a little sulphuric acid, 0·0041 grm. sulphate of lead, which corresponds to 0·0036 of the carbonate. One part of the latter salt requires accordingly 23450 parts of the above fluid for solution. The solution was mixed with sulphuretted hydrogen water; when looking through the fluid from the top of the test-cylinder, a distinct coloration was visible; but when looking through the cylinder laterally, this coloration was hardly perceptible. Traces of sulphide of lead separated after the lapse of some time.

c. In Water containing a large proportion of Nitrate of Ammonia, together with Carbonate of Ammonia and Caustic Ammonia.

A highly dilute solution of acetate of lead was mixed with nitric acid, then with carbonate of ammonia and ammonia in excess; the mixture was gently heated, and allowed to stand at rest for 8 days. The filtrate, mixed with sulphuretted hydrogen, exhibited a very distinct brownish color upon looking through it from the top of the cylinder; but this color appeared very slight only when looking through the cylinder laterally. The amount of lead dissolved was unquestionably more considerable than in *b.*

[illegible] was observed [illegible] had been added to [illegible]

[illegible] WATER (to § 83 [illegible])

[illegible] lead was [illegible] days [illegible] 42 grm. of the filtrate [illegible] consequently [illegible] part of this salt [illegible] solution.

[illegible] gen, exhibited a distinct brown [illegible], but this [illegible] appeared very [illegible]

[illegible] WATER CONTAINING SULPHURIC [illegible]

[illegible] was mixed with an excess of dilute [illegible] gently heated, and the precipitate [illegible] grm of the filtrate left [illegible] grm. [illegible] ves therefore in [illegible] parts of water [illegible] mixed with sulphuretted hydrogen [illegible] through the cylinder laterally, and very [illegible] the cylinder.

[illegible] IN WATER CONTAINING AMMONIA [illegible] § 83, *d*).

[illegible] lead was mixed with a [illegible] sulphuric acid in excess added [illegible] After [illegible] red. The filtrate was nearly [illegible] from the top of the cylinder [illegible] water.

[illegible] LEAD UPON IGNITION (to § 83 [illegible])

[illegible] atomic weight of sulphur, ERDMANN [illegible] lead loses [illegible] sulphuric acid [illegible] nt of this [illegible] method of determining lead as a sulphate [illegible] PbO, SO [illegible] the most intense [illegible] I could not perceive the slightest [illegible] loss did not amount to [illegible] grm.

[illegible] OF LEAD ON DRYING AT [illegible] (to § 8[illegible])

[illegible] from [illegible] dry, kept [illegible] time [illegible] wing numbers represent the results of the [illegible]

III. 0·8[illegible] IV. 0·8[illegible] V. 0·8[illegible]

[illegible] MERCURY AT THE COMMON TEMPERATURE [illegible] WATER (to § 84 [illegible])

[illegible] ss of mercury [illegible] and [illegible] experiments: —

[illegible] perfectly [illegible] again as [illegible] and weighed [illegible] After [illegible] the mercury [illegible] sulphuric [illegible]

[illegible]

After the lapse of 24 hours the weight had not altered in the least. I introduced the 6·4411 grm. mercury into a flask, treated it with a copious quantity of distilled water, and boiled for 15 minutes violently. I then placed the mercury again upon the watch-glass, dried it most carefully with blotting-paper, and weighed. The weight was now 6·4402 grm. Finding that a trace of mercury had adhered to the paper, I repeated the same experiment with the 6·4402 grm. After 15 minutes' boiling with water, the mercury had again lost 0·0004 grm. The remaining 6·4398 grm. were exposed to the air for 6 days (in summer, during very hot weather), after which they were found to have lost only 0·0005 grm.

55. Deportment of Sulphide of Mercury with Solution of Potassa, Sulphide of Ammonium, etc. (to § 84, *c*).

a. If recently precipitated pure sulphide of mercury is boiled with pure solution of potassa, not a trace of it dissolves in that fluid; hydrochloric acid produces no precipitate, nor even the least coloration, in the filtrate.

b. If sulphide of mercury is boiled with solution of potassa, with addition of some sulphuretted hydrogen water, sulphide of ammonium, or sulphur, complete solution is effected.

c. If freshly precipitated sulphide of mercury is digested in the cold with yellowish or very yellow sulphide of ammonium, slight, but distinctly perceptible traces are dissolved, while in the case of hot digestion, scarcely any traces of mercury can be detected in the solution.*

d. Thoroughly washed sulphide of mercury, moistened with water, suffers no alteration upon exposure to the air; at least, the fluid which I obtained by washing sulphide of mercury which had been thus exposed for 24 hours, did not manifest acid reaction, nor did it contain mercury or sulphuric acid.

56. Deportment of Oxide of Copper upon Ignition (to § 85, *b*).

Pure oxide of copper (prepared from nitrate of copper) was ignited in a platinum crucible, then cooled under a bell-jar over sulphuric acid, and finally weighed. The weight was 3·542 grm. The oxide was then most intensely ignited for 5 minutes, over a Berzelius' lamp, and weighed as before, when the weight was found unaltered; the oxide was then once more ignited for 5 minutes, but with the same result.

57. Deportment of Oxide of Copper in the air (to § 85, *b*).

A platinum crucible containing 4·3921 grm. of gently ignited oxide of copper (prepared from the nitrate) stood for 10 minutes, covered with the lid, in a warm room (in winter); the weight of the oxide of copper was found to have increased to 4·3939 grm.

The oxide of copper was then intensely ignited over a spirit-lamp; after 10 minutes' standing in the covered crucible, the weight had not perceptibly increased; after 24 hours it had increased by 0·0036 grm.

58. Deportment of Sulphide of Bismuth upon drying at 100° (to § 86, *e*).

0·4558 grm. of sulphide of bismuth prepared in the wet way were placed in the desiccator on a watch glass and allowed to stand at the common temperature. After 3 hours the weight was 0·4270, after 6 hours 0·4258, after 2 days the same.

0·3602 grm. of the sulphide of bismuth so dried was put into a water-bath, in 15 minutes it weighed 0·3596, half an hour afterwards 0·3599, in half an hour more 0·3603, in two hours 0·3626. In a second experiment the drying was kept up for 4 days, and a continual increase of weight was observed.

0·5081 grm. of sulphide of bismuth dried in the desiccator was heated in a boat in a stream of carbonic acid. After gentle ignition the weight was 0·5002, after repeated heating 0·4992. The sulphide of bismuth was visibly volatilized on ignition in the current of carbonic acid.

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[*] Comp. my experiments in the Zeitschrift f. Anal. Chem. 3, 140.

59. Deportment of Sulphide of Cadmium with Ammonia, etc. (to § 87, *c*).

Recently precipitated pure sulphide of cadmium was diffused through water, and the following experiments were made with the mixture.

a. A portion was digested cold with ammonia in excess, and filtered. The filtrate remained perfectly clear upon addition of hydrochloric acid.

b. Another portion was digested hot with excess of ammonia, and filtered. This filtrate likewise remained perfectly clear upon addition of hydrochloric acid.

c. Another portion was digested for some time with solution of cyanide of potassium, and filtered. This filtrate also remained perfectly clear upon addition of hydrochloric acid.

d. Another portion was digested with hydrosulphate of sulphide of ammonium, and filtered. The turbidity which hydrochloric acid imparted to this filtrate was pure white.

(A remark made by Wackenroder, in Buchner's Repertor. d. Pharm., xlvi. 226, induced me to make these experiments.)

60. Deportment of Precipitated Tersulphide of Antimony on Drying (to § 90, *a*).

0·2899 grm. of pure precipitated tersulphide of antimony dried in the desiccator lost, when dried at 100°, 0·0007.

0·4457 grm. of the substance dried at 100° lost, when heated to blackening in a stream of carbonic acid, 0·0011 water.

0·1932 grm. of the substance dried at 100° gave up 0·0012, when heated to blackening in a stream of carbonic acid, and after stronger heating, during which fumes of sulphide of antimony began to escape, the total loss amounted to 0·0022 grm.

0·1670 grm. of the substance dried at 100° lost 0·0005 grm. on being heated to blackening in a stream of carbonic acid.

61. Amount of Water in Hydrated Silicic Acid (to § 93, 9).

(*Experiments made by my assistant, Mr.* Lippert.)

A dilute solution of soluble glass was slowly dropped into hydrochloric acid, as long as the precipitate continued to dissolve rapidly, then the clear fluid was heated in the water-bath, till it set to a transparent jelly. This jelly was dried as far as possible with blotting paper, diffused in water, and washed by decantation till the fluid altogether ceased to give the chlorine reaction. It was then transferred to a filter, and the latter spread on blotting paper and exposed till a crumbly mass was left from the spontaneous evaporation of water. One half (I.) was dried for 8 weeks in the desiccator over sulphuric acid, with occasional trituration, the other half (II.) was dried under similar circumstances, but in a vacuum. Both were transferred to closed tubes and these were kept in the desiccator.

The weighing of the substance dried at 100° was effected between watch glasses. For the purpose of igniting the residue, it was allowed to satiate itself with aqueous vapor by exposure to the air, otherwise a considerable quantity of the substance would have been lost, then water was dropped upon it in the watch glass, then it was rinsed into a platinum crucible, dried in a water-bath, and ignited, at first cautiously, towards the end, intensely.

The substance I. contained	Expt. 1.	Expt. 2.
Water, escaping at or below 100°	4·19	9·28
" " above 100°	4·76	
Silicic acid	91·05	90·72
	100·00	100·00

Consequently the hydrate dried at 100° consists of 4·97 water and 95·03 silicic acid. In the substance dried in the desiccator the oxygen of the total water: the oxygen of the silicic acid, according to the first experiment : : 1 : 6·1, acecond experiment : : 1 : 5·86. And in the substance dried at n of the water : the oxygen of the silicic acid : : 1 : 11·5.

ance II. contained	Expt. 1.	Expt. 2.	Expt. 3.
, escaping at or below 100°	4·75	4·71	9·95
" above 100°	5·26	5·21	
cic acid	89·99	90·08	90·05
	100·00	100·00	100·00

nsequently the hydrate dried at 100° consists on the average of 5·49 water nd 94·51 silicic acid. In the substance dried in a vacuum over sulphuric acid the oxygen of the total water : the oxygen of the silicic acid—on an average : : 1 : 5·41. And in the substance dried at 100° the oxygen of the water : the oxygen of the silicic acid : : 1 : 10·43.

62. DETERMINATION OF BARYTA BY PRECIPITATION WITH CARBONATE OF AMMONIA (to § 101, 2, *a*).

0·7553 grm. pure ignited chloride of barium precipitated after § 101, 2, *a*, gave 0·7142 Ba O, C O_2, which corresponds to 0·554719 Ba O = 73·44 per cent. (100 parts of Ba Cl ought to have given 73·59 parts). The result accordingly was 99·79 instead of 100.

63. DETERMINATION OF BARYTA IN ORGANIC SALTS (to § 101, 2, *b*).

0·686 grm. racemate of baryta (2 BaO, $C_8 H_4 O_{10}$+5 aq.) treated according to § 101, 2, *b*, gave 0·408 carbonate of baryta = 0·3169 Ba O = 46·20 per cent. (calculated 46·38 per cent.) ; *i.e.*, 99·61 instead of 100.

64. DETERMINATION OF STRONTIA AS SULPHATE OF STRONTIA (to § 102, 1, *a*).

a. An aqueous solution of 1·2398 grm. Sr Cl was precipitated with sulphuric acid in excess, and the precipitated sulphate of strontia washed with water. It weighed 1·4113, which corresponds to 0·795408 Sr O = 64·15 per cent. (calculated 65·38 per cent.) ; *i.e.*, 98·12 instead of 100.
b. 1·1510 grm. Sr O, C O_2 was dissolved in excess of hydrochloric acid, the solution diluted, and then precipitated with sulphuric acid ; the precipitated Sr O, S O_3 was washed with water ; it weighed 1·4024 = 0·79039 Sr O = 68·68 per cent. (calculated 70·07 per cent.) ; *i.e.*, 98·02 instead of 100.

65. DETERMINATION OF STRONTIA AS SULPHATE, WITH CORRECTION (to § 102, 1, *a*).

The *filtrate* obtained in No. 64, *b*, weighed 190·84 grm. According to experiment No. 22, 11862 parts of water containing sulphuric acid dissolve 1 part of sulphate of strontia; therefore, 190·84 grm. dissolve 0·0161. The *washings* weighed 63·61 grm. According to experiment No. 21, 6895 parts of water dissolve 1 part of Sr O, S O_3 ; therefore, 63·61 grm. dissolve 0·0092 grm.
Adding 0·0161 and 0·0092 to the 1·4024 actually obtained, we find the total amount = 1·4277 grm., which corresponds to 0·80465 Sr O = 69·91 per cent. in Sr O, C O_2 (calculated 70·07 per cent.) ; *i.e.*, 99·77 instead of 100.

66. DETERMINATION OF STRONTIA AS CARBONATE OF STRONTIA (to § 102, 2).

1·3104 grm. chloride of strontium, precipitated according to § 102, 2, gave 1·2204 Sr O, C O_2, containing 0·8551831 Sr O=65·26 per cent. (calculated 65·38) ; *i.e.*, 99·82 instead of 100.

IN THE FOUR FOLLOWING EXPERIMENTS, AND ALSO IN No. 72, PURE AIR-dried carbonate of lime was used, in a portion of which the amount of anhydrous carbonate had been determined by very cautious heating. 0·7647 grm. left 0·7581 grm., which weight remained unaltered upon further (extremely gentle) ignition; *the air-dried carbonate contained accordingly* 55·516 *per cent. of lime.*

59. DEPORTMENT OF LIME BY PRECIPITATION
§ 87, c.

Recently was dissolved in hydrochloric
and the fol acid and alcohol, after § 103,
a. A portion was ing 0·65598 Ca O. *i.e.*, 55·31 per
trate remained instead of 100.
b. Another portion
This filtrate O₂, BY PRECIPITATION WITH
acid. WITH PURE WATER (to § 103, 2, *a*).
c. Another portion
tassium, and grm. of "the air-dried carbonate of
of hydrochl 1·1243 grm. anhydrous carbonate of
d. Another por 5 per cent. (calculated 55·51 per cent.)
and filtered
pure white
(A remark O, C O₂, BY PRECIPITATION WITH
xlvi. 22 SOLUTION (to § 103, 2, *b*, *a*).

of lime" dissolved in hydrochloric
60. DE gave 1·1682 grm. Ca O, C O₂ (reaction
ING (to § a O = 55·513 per cent. (calculated 55·516
0·28 100.
tor lost.
0·44 OXALATE (to § 103, 2, *b*, *a*).
a strea
0·19 of lime" were dissolved in hydrochloric
blacke with oxalate of ammonia and ammonia, the
fumes at 100°, until the weight remained constant.
0·0 weighed 1·2461 grm., containing 0·477879
0·1 55·516 per cent.), which gives 100·45 instead
black

6 TION OF LIME PRECIPITATED AS OXALATE (to

were taken of a solution of pure chloride of cal-
determined in the gravimetric way (by pre-
and weighing as Ca O, C O₂); in two by the
and in two by precipitation with oxalate of am-
acid in the precipitate by solution of per-
following were the results obtained:—

By the alkalimetric method.	*c.* By solution of permanganate of potassa.
0·5614	0·5613
0·5620	0·5620

a O AS Ca O, C O₂ BY PRECIPITATION AS 2 Ca O, $\bar{O}$
03, 2, *b*, *β*).

carbonate of lime" dissolved in hydrochloric acid
according to the directions of § 103, 2, *b*, *β*,
which did not manifest alkaline reaction, and the
in the least upon evaporation with carbonate of
Ca O = 55·39 per cent. (calculated 55·51), which

MAGNESIA AS 2 Mg O, P O₅ (to § 104, 2).

grm. pure anhydrous sulphate of magnesia in water,
104, 2, gave 0·9834 pyrophosphate of magnesia, con-
33·476 per cent. (calculated 33·33 per cent.), which

0·3974 2 Mg O, P O₅ = 33·43 per cent. of Mg O (cal-
100·30 instead of 100.

74. PRECIPITATION OF ACETATE OF ZINC BY SULPHURETTED HYDROGEN (to § 108, *b*).

a. A solution of pure acetate of zinc was treated with the gas in excess, allowed to stand at rest for some time, and then filtered. The filtrate was mixed with ammonia; it remained perfectly clear at first, and even after long standing a few hardly visible flakes only had separated.

b. A solution of acetate of zinc to which a tolerably large amount of acetic acid had been added previously to the precipitation with sulphuretted hydrogen, showed exactly the same deportment.

75. DETERMINATION OF IRON AS SULPHIDE (to § 113, 2).

10 c. c. of a pure solution of sesquichloride of iron was precipitated with ammonia; obtained 0·1453 $Fe_2 O_3$ =0·10171 Fe.

10 c. c. was precipitated with ammonia and sulphide of ammonium, and treated after § 113, 2, obtained 0·1596 $Fe\,S$=0·10157 Fe.

10 c. c. again yielded 0·1605 $Fe\,S$=0.1021 Fe.

76. DETERMINATION OF LEAD AS CHROMATE (to § 116, 4).

1·0083 grm. pure nitrate of lead were treated according to § 116, 4. The precipitate was collected on a weighed filter, and dried at 100°, obtained 0·9871 grm.=0·67833 $Pb\,O$. This gives 67·3 per cent. Calculation 67·4.

0·9814 nitrate of lead again yielded 0·9625 chromate=67·4 per cent.

77. DETERMINATION OF MERCURY IN THE METALLIC STATE, IN THE WET WAY, BY MEANS OF PROTOCHLORIDE OF TIN (to § 118, 1, *b*).

2·01 grm. chloride of mercury gave 1·465 grm. metallic mercury=72·88 per cent. (calculated 73·83 per cent.), which gives 98·71 instead of 100 (SCHAFFNER). The loss is not inherent in the method, *i.e.*, it does not arise from mercury evaporating during the ebullition and desiccation (Expt. No. 54); but its origin lies in the fact that one usually does not allow sufficient time for the mercury to settle quite completely, and in general is not careful enough in decanting, and drying with paper, &c.

78. DETERMINATION OF COPPER BY PRECIPITATION WITH ZINC IN A PLATINUM DISH (to § 119, 2).

30·882 grm. pure sulphate of copper were dissolved in water to 250 c. c.; 10 c. c. of the solution contained accordingly 0·31387 grm. metallic copper.

a. 10 c. c. precipitated with zinc in a platinum dish, gave 0·3140=100·06 per cent.

b. In a second experiment 10 c. c. gave 0·3138 = 100 per cent.

79. BEHAVIOR OF COPPER PRECIPITATED BY ZINC ON IGNITION IN HYDROGEN (to p. 229, foot-note).

A dilute solution of sulphate of copper was acidified with hydrochloric acid and precipitated with zinc in a platinum crucible, the precipitate was washed with water, then with alcohol, and dried at 100°. 0·7961 grm. of this was ignited for ¼ of an hour in a stream of hydrogen. It then weighed 0·7952 grm.

80. DETERMINATION OF COPPER AS SUBSULPHOCYANIDE (to § 119, 3, *b*).

0·5965 grm. of pure sulphate of copper was dissolved in a little water, and, after addition of an excess of sulphurous acid, precipitated with sulphocyanide of potassium. The well-washed precipitate, dried at 100°, weighed 0·2893, corresponding to 0·1892 $Cu\,O$=31·72 per cent. As sulphate of copper contains 31·83 per cent., this gives 99·66 instead of 100.

81. DETERMINATION OF COPPER BY DE HAEN'S METHOD (to § 119, 4, *a*).

Four 10 c. c.'s of a solution of sulphate of copper, each 10 c. c. containing 0·0254 grm. Cu, were severally mixed with iodide of potassium, then with 50 c. c. of a solution of sulphurous acid (50 c. c. corresponding to 12·94 c. c. iodine solution). After addition of starch paste, iodine solution was added until the fluid appeared blue.

[illegible].—

In *a*, 4·09
b, 3·95
c, 4·06
d, 3·95

[illegible] c. c. of iodine solution contained 0·58043 grm. iodine, this gives—

For *a*, 0·0256 Cu instead of 0·0254
" *b*, 0·0260 " "
" *c*, 0·0257 " "
" *d*, 0·0260 " "

[illegible] experiment, made with 100 c. c. of the same solution of sulphate of [illegible] gave 0·2606 instead of 0·254 of copper. Nitrate of ammonia having been [illegible] to 10 c. c. of the solution of sulphate of copper, then some dilute hydro[illegible] acid, 3·4 and 3·5 c. c. of iodine solution were required instead of 4 c. c.,—[illegible] that considerably more iodine had separated than corresponded to the [illegible] of copper.

ACTION OF SOLUTION OF CYANIDE OF POTASSIUM UPON AMMONIACAL [illegible] OF OXIDE OF COPPER (to § 119, 4, *b*).

Three 10 c. c.'s of a solution of sulphate of copper, each 10 c. c. containing [illegible] sulphate of copper, were mixed with increasing quantities of a solution [illegible], and a sufficient amount of water to equalize the degree of concen[illegible] the three portions. Solution of cyanide of potassium was then added, [illegible] drop, until the blue color had disappeared. This required the following [illegible]:—

[illegible] of sulphate [illegible] copper.	Solution of ammonia.	Water.	Solution of cyanide of potassium.
10 c. c.	4 c. c.	12 c. c.	6·7
10 c. c.	8 c. c.	8 c. c.	6·85
10 c. c.	16 c. c.	0 c. c.	7·1

[illegible] salts of ammonia also exercise some influence, as the following experi[illegible] show, which were made the next day with the same solutions:—

[illegible] $S O_3$.	Sol. $N H_3$.	Water, &c.	Sol. K Cy.
[illegible] c. c.	2 c. c.	14 c. c.	6·70
[illegible] c. c.	2 c. c.	14 c. c. sol. $N H_4 Cl$ (1 : 10)	7·40
[illegible] c. c.	6 c. c.	10 c. c. water, 4 c. c. $S O_3$ dil. (1 : 5)	7·00
[illegible] c. c.	2 c. c.	8 c. c. $N H_4 O, N O_5$ (1 : 10) 6 c. c. water	7·30

[illegible] 10 c. c.'s of solution of sulphate of copper, each 10 c. c. containing [illegible] salt, were mixed with 10 c. c.'s of a solution of sesquicarbonate [illegible], and after addition of water or of solution of neutral ammo[illegible] potassium solution was added till the blue color had vanished. [illegible]

[illegible]	[illegible] $2 N H_4 O, 3 CO_2$	c. c. Water, &c.	c. c. K Cy.
·	10	10. water	i. 16·4 ii. 16·6
·	10	10. $N H_4 O, S O_3$ (1 :10)	i. 16·9 ii. 17·1
	10	10. $N H_4 O, N O_5$ (1 : 10)	i. 17·0 ii. 17·1
	10	10. $N H_4 Cl$ (1 : 10)	i. 17·1 ii. 17·1

[illegible] 2 drops of ferrocyanide of potassium does not much assist [illegible] reaction, as the solution, which towards the end is colored [illegible] light yellow when more cyanide is added, and is not fully [illegible] addition of the same salt has been made, and it has stood [illegible]

[illegible] OF NITRATE OF BISMUTH BY CARBONATE OF AMMONIA

[illegible] of bismuth, no matter whether containing much or little free nitric acid, is mixed with water, precipitated with carbonate of ammonia and ammonia, and filtered without applying heat, the filtrate acquires, upon addition of sulphuretted hydrogen water, a blackish-brown color. But if the mixture before filtering is heated for a short time nearly to boiling, sulphuretted hydrogen fails to impart this color to the filtrate, or, at all events, the change of color is hardly visible to the eye looking through the full test-tube from the top.

84. Determination of Antimony as Sulphide (to § 125, 1).

0·559 grm. of pure air-dried tartar emetic, treated according to § 125, 1, gave 0·2902 grm. tersulphide of antimony dried at 100°, = ·2492 grm. or 44·58 per cent. of teroxide of antimony. Heated to blackening in a current of carbonic acid, the precipitate lost 0·0079 grm. (reckoned from a part to the whole), leaving accordingly 0·2823 grm. of anhydrous tersulphide of antimony, which corresponds to 0·24245 grm. or 43·37 per cent. of teroxide of antimony. As the tartar emetic contains 43·70 per cent. of teroxide of antimony, the process gives, if the precipitate is dried at 100°, 102·01; if heated to blackening, 99·22 instead of 100.

89. Determination of Phosphoric Acid as Pyrophosphate of Magnesia (to § 134, *b*, α).

1·9159 and 2·0860 grm. pure crystallized phosphate of soda, treated as directed § 134, *b*, α, gave 0·5941 and 0·6494 grm. of pyrophosphate of magnesia respectively. These give 19·83 and 19·91 per cent. of phosphoric acid in phosphate of soda, instead of 19·83 per cent.

90. Determination of Phosphoric Acid as Phosphate of Sesquioxide of Uranium (to § 134, *c*).

30 c. c. of a solution of pure phosphate of soda, treated with sulphate of magnesia, chloride of ammonium, and ammonia, as directed § 134, *b*, α, gave 0·3269 grm. of pyrophosphate of magnesia. 10 c. c. contained accordingly 0·06982 grm. of phosphoric acid.

10 c. c. of the same solution were then precipitated with acetate of sesquioxide of uranium as directed § 134, *c*. The ignited precipitate was treated with a little nitric acid, then again ignited; after cooling, it weighed 0·3478 grm. corresponding to 0·06954 grm. of phosphoric acid.

91. Determination of Free Sulphuretted Hydrogen by Means of Solution of Iodine (to § 148, I., *a*).

The experiments were made to settle the following questions:—

a. Does the quantity of iodine required remain the same for solutions of sulphuretted hydrogen of different degrees of dilution?

b. Does the equation $H S+I=H I+S$ really represent the decomposition which takes place?

The sulphuretted hydrogen water was contained in a flask closed by a doubly-perforated cork; into one aperture a siphon with pinchcock was fitted, to draw off the fluid; into the other aperture a short open tube, which did not dip into the fluid.

Question *a*.

α. About 30 c. c. of iodine solution were introduced into a flask, which was then tared; sulphuretted hydrogen water was added until the yellow color had just disappeared. The flask was then closed, weighed, starch paste added, and then solution of iodine until the fluid appeared blue.

70·2 grm. H S water required 23·4 c. c. iodine solution, 100 accordingly 33·33 c. c.

68·4 grm. required 22·7 c. c. iodine solution, 100 accordingly 33·20 c. c.

β. Same process; but the fluid was diluted with water free from air.

61·5 grm. H S water + 200 grm. water required 20·7 c. c. iodine solution, 100 accordingly 33·65 c. c.

52·4 grm. + 400 grm. water required 17·7 c. c. iodine solution, 100 accordingly 33·77.

The iodine solution contained 0·00498 iodine in 1 c. c. Considering that addition of a larger volume of water necessarily involves a slight increase in the quantity of iodine solution, these results may be considered sufficiently corresponding.

Question *b*.

According to *a*, 100 grm. of the H S water containe
ing the proportion to be 100 : 33·2.

173·6 grm. of the same water were, immediately a
drawn off into a hydrochloric acid solution of arseniou
tersulphide of arsenic acid was filtered off, dried at 1
grm. were obtained, which corresponds to 0·0381
0·02197.

The second question also is therefore answered in t

92. SOLUTION OF CHLORIDE OF MAGNESIUM DIS
(to § 154, 6).

If some chloride of calcium is added to a solution
then a little oxalate of ammonia, no precipitate is
slightly increasing the quantity of oxalate of ammo
gradually separates after some time.

If an excess of oxalate of ammonia is added, the
down, but the precipitate contains also oxalate of ma
effect the separation of the two bases by oxalate of
be added in excess; whilst, on the other hand,
magnesia, the operator must expect to precipitate so
following experiments (No. 93) clearly show.

93. SEPARATION OF LIME FROM MAGNESIA (to § 1

The fluids employed in the following experiments
ride of calcium, 10 c. c. of which corresponded to 0
tion of chloride of magnesium, containing 0·250 Mg
chloride of ammonium (1 : 8); solution of ammonia,
$\mathrm{H_2}$; solution of oxalate of ammonia (1 : 24); acetic
$\bar{\mathrm{A}}$, H O.

The precipitation was effected at the common te
of oxalate of lime was filtered off after 20 hours.

a. Influence of the degree of dilution.

α. 10 c. c. Mg Cl, 10 c. c. Ca Cl, 10 c. c. $\mathrm{NH_4}$
water, 20 c. c. $\mathrm{2\,NH_4\,O,\,\bar{O}}$. Result, 0·5705 Ca
β. Same as *α*, with 150 c. c. water instead of 5
O, $\mathrm{CO_2}$.

b. Influence of excess of ammonia.
Same as *a*, *β* + 10 c. c. $\mathrm{NH_4O}$. Result, 0·5614

c. Influence of excess of chloride of ammonium.
Same as *a*, *β* + 40 c. c. $\mathrm{NH_4Cl}$. Result, 0·5652

d. Influence of excess of ammonia and chloride of a
Same as *a*, *β* + 30 c. c. $\mathrm{NH_4Cl}$ + 10 c. c. $\mathrm{NH_4O}$.

e. Influence of free acetic acid.
Same as *a*, *β*, only with 6 drops $\bar{\mathrm{A}}$, instead of th
0·5594 grm.

f. Influence of excess of oxalate of ammonia, in fe
Same as *a*, *β* + 20 c. c. $\mathrm{2\,NH_4\,O,\,\bar{O}}$. Result, 0·5

g. Influence of excess of oxalate of ammonia, in str
Same as *a*, *β*, + 10 c. c. $\mathrm{NH_4O}$ + 20 c. c. $\mathrm{2\,NH_4O}$

h. Influence of excess of oxalate of ammonia, in pre
$\mathrm{NH_4O}$.
Same as *a*, *β*, + 10 $\mathrm{NH_4\,O}$ + 30 $\mathrm{NH_4Cl}$ + 20 2
grm.

i. Influence of excess of oxalate of ammonia, in
with $\bar{\mathrm{A}}$.
Same as *a*, *β*,—4 drops $\mathrm{NH_4O}$ + 6 drops $\bar{\mathrm{A}}$ + 20
0·5661 grm.

Consequently, when a notable amount of magnesia
chance of oxalate of magnesia, or oxalate of magnesia
along with the oxalate of lime.

Another series of experiments in which a solution of oxalate of magnesia in hydrochloric acid was mixed with ammonia under varying circumstances, proved also that, in presence of a notable quantity of magnesia, oxalate of magnesia, or oxalate of magnesia and ammonia, will always separate after standing for some time, no matter whether in a cold or a warm place.

In a third series of experiments, the separation was effected by double precipitation, in accordance with **29**. The same solutions were employed as in the first series, with the exception of the chloride of magnesium, for which a solution was substituted containing 0·2182 grm. Mg O, in 10 c. c.

10 c. c. Ca Cl + 30 c. c. Mg Cl, + 20 c. c. NH_4Cl, + 300 c. c. water, + 6 drops ammonia, + a sufficient excess of oxalate of ammonia. Results, in two experiments, 0·5621 and 0·5652, mean 0·5636, instead of 0·5618 Ca O, CO_2; also 0·6660 and 0·6489 Mg O, mean 0·6574, instead of 0·6546.

94. Separation of Iodine from Chlorine by Pisani's Method (to § 169, **204**).

0·2338 grm. iodide of potassium, dissolved in water, + ½ c. c. of solution of iodide of starch, required 14 c. c. of decinormal silver solution = 0·2322 grm. iodide of potassium.

0·3025 grm. iodide of potassium, mixed with about double the quantity of chloride of sodium, required 18·2 c. c. silver solution = 0·3021 K I.

0·2266 grm. iodide of potassium, mixed with about 100 times as much chloride of sodium, required 13·7 c. c. silver solution = 0·2272 K I.

95. Separation of Iodine from Bromine, by Pisani's Method (to § 169, **209**).

0·3198 grm. iodide of potassium, mixed with double the quantity of bromide of potassium, required 19·2 c. c. of decinormal silver solution = 0·3187 K I.

99. Chlorimetrical Experiments (to § 213).

10 grm. of chloride of lime were rubbed up with water to one litre, with which the following experiments were made:—

a. By Penot's method (§ 212); obtained 23·5 and 23·5 per cent.
b. By means of iron (§ 213, modification); obtained 23·6 per cent.
c. By Bunsen's method (p. 508, C); results, 23·6—23·6 per cent.

100. Drying of Manganese (to § 214, I.)

Four small pans, containing each 8 grm. of manganese of 53 per cent., were first heated in the water-bath. After 3 hours, I. had lost 0·145; after 6 hours, II. 0·15; after 9 hours, III. 0·15; after 12 hours, IV. 0·15. grm. I. and II. having been left standing, loosely covered, in the room for 12 hours, II. was found to weigh exactly as much as at first; I. wanted only 0·01 grm. of the original weight.

The four pans were now heated for two hours to 120°. After cooling, they were found to have lost each 0·180 of the original weight. I. and II. having been left standing, loosely covered, in the room for 60 hours, were found to have again acquired their original weight by attracting moisture. III. and IV. were heated for 2 hours to 150°. The loss of weight in both cases was 0·215 grm. Having been left standing, loosely covered, in the room for 72 hours, both were found to weigh 0·05 less than at first. Assuming the hygroscopic moisture expelled to be re-absorbed by standing in the air, this shows that at 150° a little chemically combined water escapes along with the moisture, and accordingly that the temperature must not exceed 120°.

My experiments will be found described in detail in Dingler's polyt. Journ., 135, 277 et seq.

TABLES FOR THE CALCULATION OF ANALYSES.

TABLE I.

EQUIVALENTS OF THE ELEMENTS CONSIDERED IN THE PRESENT WORK.*

Aluminium	Al	13·75	(Dumas)
Antimony	Sb	122·00	(Dumas)
Arsenic	As	75·00	(Pelouze, Berzelius)
Barium	Ba	68·50	(Dumas)
Bismuth	Bi	208·00†	(Schneider)
Boron	B	11·00	(Berzelius)
Bromine	Br	80·00	(Marignac)
Cadmium	Cd	56·00	(C. v. Hauer)
Cæsium	Cs	133·00	(Johnson and Allen, Bunsen)
Calcium	Ca	20·00	(Dumas, Erdmann and Marchand)
Carbon	C	6·00	(Dumas, Erdmann and Marchand)
Chlorine	Cl	35·46	(Marignac, Stas)
Chromium	Cr	26·24	(Berlin, Péligot)
Cobalt	Co	29·50‡	(Rothoff, Dumas)
Copper	Cu	31·70	(Erdmann and Marchand)
Fluorine	Fl	19·00	(Louyet)
Gold	Au	196·00	(Comp. Strecker, loc. cit.)
Hydrogen	H	1·00	(Dumas)
Iodine	I	127·00	(Marignac, Dumas)
Iron	Fe	28·00	(Erdmann and Marchand)
Lead	Pb	103·50	(Berzelius, Dumas)
Lithium	Li	7·00	(C. Diehl, Troost)
Magnesium	Mg	12·00	(Marchand and Scheerer)
Manganese	Mn	27·50	(v. Hauer, Dumas)
Mercury	Hg	100·00	(Erdmann and Marchand)
Molybdenum	Mo	46·00|	(Berlin)
Nickel	Ni	29·50¶	(Rothoff, Marignac, Dumas)
Nitrogen	N	14·00	(Marignac)
Oxygen	O	8·00	
Palladium	Pd	53·00	(Berzelius, comp. Strecker, loc. cit.)
Phosphorus	P	31·00	(Schrötter)
Platinum	Pt	98·94	(Andrews)
Potassium	K	39·11	(Marignac, Stas)
Rubidium	Rb	85·40	(Bunsen, Piccard)
Selenium	Se	39·5**	(Berzelius, Sacc, Erdmann, and Marchand—mean)
Silicon	Si	14·00††	(Dumas)
Silver	Ag	107·97	(Marignac)
Sodium	Na	23·00	(Pelouze, Stas)
Strontium	Sr	43·75	(Dumas)
Sulphur	S	16·00	(Erdmann and Marchand)
Thallium	Tl	203·00‡‡	(Crookes)
Tin	Sn	59·00‖	(Dumas)
Titanium	Ti	25·00	(Pierre)
Uranium	Ur	59·40¶¶	(Ebelmen)
Zinc	Zn	32·53	(Axel Erdmann)

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[*] It has been necessary to alter the numbers in some cases where no new special experiments have been made. This arose from the fact that the numbers in question were deduced from other equivalents which have since been corrected. Those who are curious in the matter of equivalents should refer to Handwörterbuch der reinen und angewandten Chemie, 2 Aufl. Bd. II. 463, article Atomgewichte, by A. Strecker. With respect to the equivalents that have recently been redetermined, comp. Zeitschrift f. Anal. Chem.

[†] Dumas makes 210·00.

[‡] W. J. Russell found 29·37. (Journ. Chem. Soc. (2). I. 51.)

[|] Dumas makes it 48·00.

[¶] W. J. Russell found 29·37 (loc. cit.).

[**] Dumas found 39·75.

[††] Silicic Acid—Si O_2.

[‡‡] After Lamy 204·00.

[‖] After Mulder 58·00.

[¶¶] Comp. p. 141, note †.

TABLE II.

COMPOSITION OF THE BASES AND OXYGEN ACIDS.

a. BASES.

GROUP I.

Caesia	Cs . . .	133·00 . .	94·33
	O . . .	8·00 . .	5·67
	Cs O . .	141·00 . .	100·00
Rubidia	Rb . . .	85·40 . .	91·43
	O . . .	8·00 . .	8·57
	Rb O . .	93·40 . .	100·00
Potassa	K . . .	39·11 . .	83·02
	O . . .	8·00 . .	16·98
	KO . . .	47·11 . .	100·00
Soda	Na . . .	23·00 . .	74·19
	O . . .	8·00 . .	25·81
	Na O . .	31·00 . .	100·00
Lithia	Li . . .	7·00 . .	46·67
	O . . .	8·00 . .	53·33
	Li O . .	15·00 . .	100·00
Oxide of Ammonium	NH_4 . .	18·00 . .	69·23
	O . . .	8·00 . .	30·77
	NH_4O . .	26·00 . .	100·00

GROUP II.

Baryta	Ba . . .	68·50 . .	89·54
	O . . .	8·00 . .	10·46
	Ba O . .	76·50 . .	100·00
Strontia	Sr . . .	43·75 . .	84·54
	O . . .	8·00 . .	15·46
	Sr O . .	51·75 . .	100·00
Lime	Ca . . .	20·00 . .	71·43
	O . . .	8·00 . .	28·57
	Ca O . .	28·00 . .	100·00
Magnesia	Mg . . .	12·00 . .	60·03
	O . . .	8·00 . .	39·97
	Mg O . .	20·00 . .	100·00

GROUP III.

Alumina	Al_2	27·50	53·40
	O_3	24·00	46·60
	Al_2O_3	51·50	100·00
Sesquioxide of Chromium	Cr_2	52·48	68·62
	O_3	24·00	31·38
	Cr_2O_3	76·48	100·00

GROUP IV.

Oxide of Zinc	Zn	32·53	80·26
	O	8·00	19·74
	ZnO	40·53	100·00
Protoxide of Manganese	Mn	27·50	77·46
	O	8·00	22·54
	MnO	35·50	100·00
Sesquioxide of Manganese	Mn_2	55·00	69·62
	O_3	24·00	30·38
	Mn_2O_3	79·00	100·00
Protoxide of Nickel	Ni	29·50	78·67
	O	8·00	21·33
	NiO	37·50	100·00
Protoxide of Cobalt	Co	29·50	78·67
	O	8·00	21·33
	CoO	37·50	100·00
Sesquioxide of Cobalt	Co_2	59·00	71·08
	O_3	24·00	28·92
	Co_2O_3	83·00	100·00
Protoxide of Iron	Fe	28·00	77·78
	O	8·00	22·22
	FeO	36·00	100·00
Sesquioxide of Iron	Fe_2	56·00	70·00
	O_3	24·00	30·00
	Fe_2O_3	80·00	100·00

GROUP V.

Oxide of Silver	Ag	107·97	93·10
	O	8·00	6·90
	AgO	115·97	100·00

Oxide of Lead	Pb	103·50	92·83
	O	8·00	7·17
	PbO	111·50	100·00
Suboxide of Mercury	Hg_2	200·00	96·15
	O	8·00	3·85
	Hg_2O	208·00	100·00
Oxide of Mercury	Hg	100·00	92·59
	O	8·00	7·41
	HgO	108·00	100·00
Suboxide of Copper	Cu_2	63·40	88·80
	O	8·00	11·20
	Cu_2O	71·40	100·00
Oxide of Copper	Cu	31·70	79·85
	O	8·00	20·15
	CuO	39·70	100·00
Teroxide of Bismuth	Bi	208·00	89·66
	O_3	24·00	10·34
	BiO_3	232·00	100·00
Oxide of Cadmium	Cd	56·00	87·50
	O	8·00	12·50
	CdO	64·00	100·00

GROUP VI.

Teroxide of Gold	Au	196·00	89·09
	O_3	24·00	10·91
	AuO_3	220·00	100·00
Binoxide of Platinum	Pt	98·94	86·08
	O_2	16·00	13·92
	PtO_2	114·94	100·00
Teroxide of Antimony	Sb	122·00	83·56
	O_3	24·00	16·44
	SbO_3	146·00	100·00
Protoxide of Tin	Sn	59·00	88·06
	O	8·00	11·94
	SnO	67·00	100·00
Binoxide of Tin	Sn	59·00	78·67
	$O.$	16·00	21·33
	$SnO.$	75·00	100·00

Arsenious acid	As	75·00	75·76
	O_3	24·00	24·24
	AsO_3	99·00	100·00
Arsenic acid	As	75·00	65·22
	O_5	40·00	34·78
	AsO_5	115·00	100·00

b. ACIDS.

Chromic acid	Cr	26·24	52·23
	O_3	24·00	47·77
	CrO_3	50·24	100·00
Sulphuric acid	S	16·00	40·00
	O_3	24·00	60.00
	SO_3	40·00	100·00
Phosphoric acid	P	31·00	43·66
	O_5	40·00	56·34
	PO_5	71·00	100·00
Boracic acid	B	11·00	31·43
	O_3	24·00	68·57
	BO_3	35·00	100·00
Oxalic acid	C_4	24·00	33·33
	O_6	48·00	66·67
	C_4O_6	72·00	100·00
Carbonic acid	C	6·00	27·27
	O_2	16·00	72·73
	CO_2	22·00	100·00
Silicic acid	Si	14·00	46·67
	O_2	16·00	53·33
	SiO_2	30·00	100·00
Nitric acid	N	14·00	25·93
	O_5	40·00	74·07
	NO_5	54·00	100·00
Chloric acid	Cl	35·46	46·99
	O_5	40·00	53·01
	ClO_5	75·46	100·00

TABLE III.

REDUCTION OF COMPOUNDS FOUND TO CONSTITUENTS SOUGHT BY SIMPLE MULTIPLICATION OR DIVISION.

This Table contains only some of the more frequently occurring compounds; the formulæ preceded by ! give absolutely accurate results. The Table may also be extended to other compounds, by proceeding according to the instructions given in § 199.

FOR INORGANIC ANALYSIS.

CARBONIC ACID.

! Carbonate of lime × 0·44=Carbonic acid.

CHLORINE.

Chloride of silver × 0·24724=Chlorine.

COPPER.

Oxide of copper × 0·79849=Copper.

IRON.

! Sesquioxide of iron × 0·7=2 Iron.
! Sesquioxide of iron × 0·9=2 Protoxide of iron.

LEAD.

Oxide of lead × 0·9283=Lead.

MAGNESIA.

Pyrophosphate of magnesia × 0·36036=2 Magnesia.

MANGANESE.

Protosesquioxide of manganese × 0·72052=3 Manganese.
Protosesquioxide of manganese × 0·93013=3 Protoxide of manganese.

PHOSPHORIC ACID.

Pyrophosphate of magnesia × 0·6396=Phosphoric acid.
Phosphate of sesquioxide of uranium $(2\,Ur_2O_3, PO_5)$ × 0·1991=Phosphoric acid.

POTASSA.

Chloride of potassium × 0·52445=Potassium.
Sulphate of potassa × 0·5408=Potassa.

$$\left.\begin{array}{c}\text{Potassio-bichloride of platinum} \times 0·30507\\ \text{or}\\ \dfrac{\text{Potassio-bichloride of platinum}}{3·275}\end{array}\right\}=\text{Chloride of potassium.}$$

$$\left.\begin{array}{c}\text{Potassio-bichloride of platinum} \times 0{\cdot}19272 \\ \text{or} \\ \dfrac{\text{Potassio-bichloride of platinum}}{5{\cdot}188}\end{array}\right\} = \text{Potassa.}$$

SODA.

Chloride of sodium × 0·5302=Soda.
Sulphate of soda × 0·43658=Soda.

SULPHUR.

Sulphate of baryta × 0·13734=Sulphur.

SULPHURIC ACID

Sulphate of baryta × 0·34335=Sulphuric acid.

FOR ORGANIC ANALYSIS.

CARBON.

$$\left.\begin{array}{c}\text{Carbonic acid} \times 0{\cdot}2727 \\ \text{or} \\ \dfrac{\text{Carbonic acid}}{3{\cdot}666} \\ \text{or} \\ \dfrac{\text{Carbonic acid} \times 3}{11}\end{array}\right\} = \text{Carbon.}$$

HYDROGEN.

$$\left.\begin{array}{c}\text{Water} \times 0{\cdot}11111 \\ \text{or} \\ \dfrac{\text{Water}}{9}\end{array}\right\} = \text{Hydrogen.}$$

NITROGEN.

Ammonio-bichloride of platinum × 0·06269=Nitrogen.
Platinum × 0·1415=Nitrogen.

TABLE

Showing the Amount of the

Number of the

Elements.	Found.	Sought.	1
Aluminium..	Alumina $Al_2 O_3$	Aluminium Al_2	0·53398
(Ammonium)	Chloride of ammonium $N H_4 Cl$	Ammonia $N H_3$	0·31804
	Ammonio-bichloride of platinum $N H_4 Cl, Pt Cl_2$	Oxide of ammonium $N H_4 O$	0·11644
	Ammonio-bichloride of platinum $N H_4 Cl, Pt Cl_2$	Ammonia $N H_3$	0·07614
Antimony...	Teroxide of antimony $Sb O_3$	Antimony Sb	0·83562
	Tersulphide of antimony $Sb S_3$	Antimony Sb	0·71765
	Tersulphide of antimony $Sb S_3$	Teroxide of antimony $Sb O_3$	0·85882
	Antimonious acid $Sb O_4$	Teroxide of antimony $Sb O_3$	0·94805
Arsenic.....	Arsenious acid $As O_3$	Arsenic As	0·75758
	Arsenic acid $As O_5$	Arsenic As	0·65217
	Arsenic acid $As O_5$	Arsenious acid $As O_3$	0·86087
	Tersulphide of arsenic $As S_3$	Arsenious acid $As O_3$	0·80488
	Tersulphide of arsenic $As S_3$	Arsenic acid $As O_5$	0·93496
	Arseniate of ammonia and magnesia $2 Mg O, N H_4 O, As O_5 + aq$	Arsenic acid $As O_5$	0·60526
	Arseniate of ammonia and magnesia $2 Mg O, N H_4 O, As O_5 + aq$	Arsenious acid $As O_3$	0·52105
Barium.....	Baryta Ba O	Barium Ba	0·89542
	Sulphate of baryta $Ba O, S O_3$	Baryta Ba O	0·65665
	Carbonate of baryta $Ba O, C O_2$	Baryta Ba O	0·77665
	Silico-fluoride of barium $Ba Fl, Si Fl_2$	Baryta Ba O	0·54839
Bismuth.....	Teroxide of bismuth $Bi O_3$	Bismuth Bi	0·89655
Boron.......	Boracic acid $B O_3$	Boron B	0·31429
Bromine.....	Bromide of silver Ag Br	Bromine Br	0·42560
Cadmium....	Oxide of cadmium Cd O	Cadmium Cd	0·87500
Calcium.....	Lime Ca O	Calcium Ca	0·71429
	Sulphate of lime $Ca O, S O_3$	Lime Ca O	0·41176
	Carbonate of lime $Ca O, C O_2$	Lime Ca O	0·56000
Carbon......	Carbonic acid $C O_2$	Carbon C	0·27273

IV.

Constituent sought for every
Compound found.

2	3	4	5	6	7	8	9
1·06796	1·60194	2·13592	2·66990	3·20389	3·73787	4·27185	4·80583
0·63608	0·95413	1·27217	1·59021	1·90825	2·22629	2·54433	2·86237
0·23288	0·34932	0·46576	0·58220	0·69864	0·81508	0·93152	1·04796
0·15228	0·22842	0·30456	0·38070	0·45684	0·53299	0·60913	0·68527
1·67123	2·50685	3·34247	4·17808	5·01370	5·84932	6·68194	7·52055
1·43529	2·15294	2·87059	3·58834	4·30588	5·02353	5·74118	6·45882
1·71765	2·57647	3·43530	4·29412	5·15294	6·01177	6·87059	7·72942
1·89610	2·84416	3·79221	4·74026	5·68831	6·63636	7·58442	8·53247
1·51516	2·27274	3·03032	3·78790	4·54548	5·30306	6·06064	6·81822
1·30435	1·95652	2·60870	3·26087	3·91304	4·56522	5·21739	5·86957
1·72174	2·58261	3·44348	4·30435	5·16521	6·02608	6·88695	7·74782
1·60975	2·41463	3·21951	4·02439	4·82927	5·63415	6·43902	7·24390
1·86992	2·80488	3·73984	4·67480	5·60975	6·54471	7·47967	8·41463
1·21053	1·81579	2·42105	3·02631	3·63158	4·23684	4·84210	5·44737
1·04210	1·56316	2·08421	2·60526	3·12631	3·64736	4·16842	4·68947
1·79085	2·68627	3·58170	4·47712	5·37255	6·26797	7·16340	8·05882
1·31330	1·96996	2·62661	3·28326	3·93991	4·59656	5·25322	5·90987
1·55330	2·32995	3·10660	3·88325	4·65990	5·43655	6·21320	6·98985
1·09677	1·64516	2·19355	2·74194	3·29032	3·83871	4·38710	4·93548
1·79310	2·68965	3·58620	4·48275	5·37930	6·27586	7·17240	8·06895
0·62857	0·94286	1·25714	1·57143	1·88572	2·20000	2·51429	2·82857
0·85120	1·27680	1·70240	2·12800	2·55360	2·97920	3·40480	3·83040
1·75000	2·62500	3·50000	4·37500	5·25000	6·12500	7·00000	7·87500
1·42857	2·14286	2·85714	3·57143	4·28571	5·00000	5·71429	6·42857
0·82353	1·23529	1·64706	2·05882	2·47059	2·88235	3·29412	3·70588
1·12000	1·68000	2·24000	2·80000	3·36000	3·92000	4·48000	5·04000
0·54546	0·81818	1·09091	1·36364	1·63636	1·90909	2·18181	2·45455

TABLE IV.

Elements.	Found.	Sought.	1
Carbon.......	Carbonate of lime $Ca\,O, C\,O_2$	Carbonic acid $C\,O_2$	0·44000
Chlorine.....	Chloride of silver $Ag\,Cl$	Chlorine Cl	0·24724
	Chloride of silver $Ag\,Cl$	Hydrochloric acid $H\,Cl$	0·25421
Chromium...	Sesquioxide of chromium $Cr_2\,O_3$	Chromium Cr_2	0·68619
	Sesquioxide of chromium $Cr_2\,O_3$	Chromic acid $2\,Cr\,O_3$	1·31381
	Chromate of lead $Pb\,O, Cr\,O_3$	Chromic acid $Cr\,O_3$	0·31062
Cobalt......	Cobalt Co	Protoxide of cobalt $Co\,O$	1·27119
	Sulphate of protoxide of cobalt $Co\,O, S\,O_3$	Protoxide of cobalt $Co\,O$	0·48387
	Sulphate of cobalt + sulphate of potassa $2\,(Co\,O, S\,O_3) + 3\,(K\,O. S\,O_3)$	Protoxide of cobalt $2\,Co\,O$	0·18015
	Sulphate of cobalt + sulphate of potassa $2\,(Co\,O, S\,O_3) + 3\,(K\,O, S\,O_3)$	Cobalt $2\,Co$	0·14171
Copper......	Oxide of copper $Cu\,O$	Copper Cu	0·79849
	Subsulphide of copper $Cu_2\,S$	Copper Cu_2	0·79849
Fluorine.....	Fluoride of calcium $Ca\,Fl$	Fluorine Fl	0·48718
	Fluoride of silicon $Si\,Fl_3$	Fluorine Fl_3	0·73077
Hydrogen...	Water $H\,O$	Hydrogen H	0·11111
Iodine.......	Iodide of silver $Ag\,I$	Iodine I	0·54049
	Protiodide of palladium $Pd\,I$	Iodine I	0·70556
Iron.........	Sesquioxide of iron $Fe_2\,O_3$	Iron Fe_2	0·70000
	Sesquioxide of iron $Fe_2\,O_3$	Protoxide of iron $2\,Fe\,O$	0·90000
	Sulphide of iron $Fe\,S$	Iron Fe	0·63636
Lead........	Oxide of lead $Pb\,O$	Lead Pb	0·92825
	Sulphate of lead $Pb\,O, S\,O_3$	Oxide of lead $Pb\,O$	0·73597
	Sulphate of lead $Pb\,O, S\,O_3$	Lead Pb	0·68317
	Sulphide of lead $Pb\,S$	Oxide of lead $Pb\,O$	0·93305
Lithium.....	Carbonate of lithia $Li\,O, C\,O_2$	Lithia $Li\,O$	0·40541
	Sulphate of lithia $Li\,O, S\,O_3$	Lithia $Li\,O$	0·27273
	Basic phosphate of lithia $3\,Li\,O, P\,O_5$	Lithia $3\,Li\,O$	0·38793

(continued).

2	3	4	5	6	7	8	9
0·88000	1·32000	1·76000	2·20000	2·64000	3·08000	3·52000	3·96000
0·49448	0·74172	0·98896	1·23620	1·48344	1·73068	1·97792	2·22516
0·50842	0·76263	1·01684	1·27105	1·52526	1·77947	2·03368	2·28789
1·37238	2·05858	2·74477	3·43096	4·11715	4·80334	5·48954	6·17573
2·62762	3·94142	5·25523	6·56904	7·88285	9·19666	10·51046	11·82427
0·62124	0·93187	1·24249	1·55311	1·86373	2·17435	2·48498	2·79560
2·54237	3·81356	5·08474	6·35593	7·62712	8·89830	10·16949	11·44067
0·96774	1·45161	1·93548	2·41935	2·90323	3·38710	3·87097	4·35484
0·36029	0·54044	0·72058	0·90073	1·08088	1·26102	1·44117	1·62131
0·28343	0·42514	0·56686	0·70857	0·85029	0·99200	1·13372	1·27543
1·59698	2·39547	3·19396	3·99244	4·79093	5·58942	6·38791	7·18640
1·59698	2·39547	3·19396	3·99244	4·79093	5·58942	6·38791	7·18640
0·97436	1·46154	1·94872	2·43590	2·92307	3·41027	3·89743	4·38461
1·46154	2·19231	2·92308	3·65385	4·38461	5·11538	5·84615	6·57692
0·22222	0·33333	0·44444	0·55555	0·66667	0·77778	0·88889	1·00000
1·08099	1·62148	2·16198	2·70247	3·24297	3·78346	4·32396	4·86445
1·41111	2·11667	2·82222	3·52778	4·23334	4·93889	5·64445	6·35000
1·40000	2·10000	2·80000	3·50000	4·20000	4·90000	5·60000	6·30000
1·80000	2·70000	3·60000	4·50000	5·40000	6·30000	7·20000	8·10000
1·27273	1·90909	2·54546	3·18182	3·81818	4·45455	5·09091	5·72728
1·85650	2·78475	3·71300	4·64126	5·56951	6·49776	7·42601	8·35426
1·47195	2·20792	2·94390	3·67987	4·41584	5·15182	5·88779	6·62377
1·36634	2·04950	2·73267	3·41584	4·09901	4·78218	5·46534	6·14851
1·86611	2·79916	3·73222	4·66527	5·59832	6·53138	7·46443	8·39749
0·81081	1·21622	1·62162	2·02703	2·43243	2·83784	3·24324	3·64865
0·54545	0·81818	1·09091	1·36364	1·63636	1·90909	2·18182	2·45454
0·77586	1·16379	1·55172	1·93966	2·32759	2·71552	3·10345	3·49138

TABLE IV.

Elements.	Found.	Sought.	1
Magnesium..	Magnesia MgO	Magnesium Mg	0·60030
	Sulphate of magnesia MgO, SO_3	Magnesia MgO	0·33350
	Pyrophosphate of magnesia $2MgO, PO_5$	Magnesia $2MgO$	0·36036
Manganese..	Protoxide of manganese MnO	Manganese Mn	0·77465
	Protosesquioxide of manganese $MnO+Mn_2O_3$	Manganese Mn_3	0·72053
	Sesquioxide of manganese Mn_2O_3	Manganese Mn_2	0·69620
	Sulphate of protoxide of manganese MnO, SO_3	Protoxide of manganese MnO	0·47020
	Sulphide of manganese MnS	Protoxide of manganese MnO	0·81609
	Sulphide of manganese MnS	Manganese Mn	0·63218
Mercury.....	Mercury Hg_2	Suboxide of mercury Hg_2O	1·04000
	Mercury Hg	Oxide of mercury HgO	1·08000
	Subchloride of mercury Hg_2Cl	Mercury Hg_2	0·84940
	Sulphide of mercury HgS	Mercury Hg	0·86207
Nickel......	Protoxide of nickel NiO	Nickel Ni	0·78667
Nitrogen....	Ammonio-bichloride of platinum $NH_4Cl, PtCl_2$	Nitrogen N	0·06071
	Platinum Pt	Nitrogen N	0·14155
	Sulphate of baryta BaO, SO_3	Nitric acid NO_5	0·46352
	Cyanide of silver AgC_2N	Cyanogen C_2N	0·19410
	Cyanide of silver AgC_2N	Hydrocyanic acid HC_2N	0·20156
Oxygen......	Alumina Al_2O_3	Oxygen O_3	0·46602
	Teroxide of antimony SbO_3	Oxygen O_3	0·16438
	Arsenious acid AsO_3	Oxygen O_3	0·24242
	Arsenic acid AsO_5	Oxygen O_5	0·34783
	Baryta BaO	Oxygen O	0·10458
	Teroxide of bismuth BiO_3	Oxygen O_3	0·10345
	Oxide of cadmium CdO	Oxygen O	0·12500
	Sesquioxide of chromium Cr_2O_3	Oxygen O_3	0·31381
	Protoxide of cobalt CoO	Oxygen O	0·21333

(*continued*).

2	3	4	5	6	7	8	9
1·20061	1·80091	2·40121	3·00151	3·60182	4·20212	4·80242	5·40273
0·66700	1·00051	1·33401	1·66751	2·00101	2·33451	2·66802	3·00152
0·72072	1·08108	1·44144	1·80180	2·16216	2·52252	2·88288	3·24324
1·54930	2·32394	3·09859	3·87324	4·64789	5·42254	6·19718	6·97183
1·44105	2·16157	2·88210	3·60262	4·32314	5·04367	5·76419	6·48472
1·39241	2·08861	2·78481	3·48102	4·17722	4·87342	5·56962	6·26583
0·94040	1·41060	1·88080	2·35099	2·82119	3·29139	3·76159	4·23179
1·63218	2·44828	3·26437	4·08046	4·89655	5·71264	6·52874	7·34483
1·26437	1·89655	2·52874	3·16092	3·79310	4·42529	5·05747	5·68966
2·08000	3·12000	4·16000	5·20000	6·24000	7·28000	8·32000	9·36000
2·16000	3·24000	4·32000	5·40000	6·48000	7·56000	8·64000	9·72000
1·69880	2·54820	3·39760	4·24701	5·09641	5·94581	6·79521	7·64461
1·72414	2·58621	3·44828	4·31034	5·17241	6·03448	6·89655	7·75862
1·57333	2·36000	3·14667	3·93333	4·72000	5·50667	6·29334	7·08000
0·12542	0·18812	0·25083	0·31354	0·37625	0·43896	0·50166	0·56437
0·28310	0·42464	0·56619	0·70774	0·84929	0·99084	1·13238	1·27393
0·92704	1·39056	1·85408	2·31760	2·78111	3·24463	3·70815	4·17167
0·38820	0·58230	0·77640	0·97050	1·16460	1·35870	1·55280	1·74690
0·40312	0·60468	0·80624	1·00780	1·20936	1·41092	1·61248	1·81404
0·93204	1·39806	1·86408	2·33010	2·79611	3·26213	3·72815	4·19417
0·32877	0·49315	0·65754	0·82192	0·98630	1·15069	1·31507	1·47946
0·48484	0·72726	0·96968	1·21210	1·45452	1·69694	1·93936	2·18178
0·69565	1·04348	1·39130	1·73913	2·08696	2·43478	2·78261	3·13043
0·20915	0·31373	0·41830	0·52288	0·62745	0·73203	0·83660	0·94118
0·20690	0·31035	0·41380	0·51725	0·62070	0·72415	0·82760	0·93105
0·25000	0·37500	0·50000	0·62500	0·75000	0·87500	1·00000	1·12500
0·62762	0·94143	1·25524	1·56905	1·88286	2·19667	2·51048	2·82429
0·42667	0·64000	0·85333	1·06667	1·28000	1·49333	1·70666	1·92000

TABLE IV.

Elements.	Found.	Sought.	1
Oxygen......	Oxide of copper $Cu\,O$	Oxygen O	0·20151
	Protoxide of iron $Fe\,O$	Oxygen O	0·22222
	Sesquioxide of iron $Fe_2\,O_3$	Oxygen O_3	0·30000
	Oxide of lead $Pb\,O$	Oxygen O	0·07175
	Lime $Ca\,O$	Oxygen O	0·28571
	Magnesia $Mg\,O$	Oxygen O	0·39970
	Protoxide of manganese $Mn\,O$	Oxygen O	0·22535
	Protosesquioxide of manganese $Mn\,O + Mn_2\,O_3$	Oxygen O_4	0·27947
	Sesquioxide of manganese $Mn_2\,O_3$	Oxygen O_3	0·30380
	Suboxide of mercury $Hg_2\,O$	Oxygen O	0·03846
	Oxide of mercury $Hg\,O$	Oxygen O	0·07407
	Protoxide of nickel $Ni\,O$	Oxygen O	0·21333
	Potassa $K\,O$	Oxygen O	0·16983
	Silicic acid $Si\,O_3$	Oxygen O_3	0·53333
	Oxide of silver $Ag\,O$	Oxygen O	0·06898
	Soda $Na\,O$	Oxygen O	0·25810
	Strontia $Sr\,O$	Oxygen O	0·15459
	Binoxide of tin $Sn\,O_2$	Oxygen O_2	0·21333
	Water HO	Oxygen O	0·88889
	Oxide of zinc $Zn\,O$	Oxygen O	0·19740
Phosphorus..	Phosphoric acid $P\,O_5$	Phosphorus P	0·43662
	Pyrophosphate of magnesia $2\,Mg\,O,\,P\,O_5$	Phosphoric acid $P\,O_5$	0·63964
	Phosphate of sesquioxide of iron $Fe_2\,O_3,\,P\,O_5$	Phosphoric acid $P\,O_5$	0·47020
	Phosphate of silver $3\,Ag\,O,\,P\,O_5$	Phosphoric acid $P\,O_5$	0·16949
	Phosphate of sesquioxide of uranium $2\,Ur_2\,O_3,\,P\,O_5$	Phosphoric acid $P\,O_5$	0·19910
	Pyrophosphate of silver $2\,Ag\,O,\,P\,O_5$	Phosphoric acid $P\,O_5$	0·23437
Potassium...	Potassa $K\,O$	Potassium K	0·83018
	Sulphate of potassa $K\,O,\,S\,O_3$	Potassa $K\,O$	0·54080

(*continued*).

2	3	4	5	6	7	8	9
0·40302	0·60453	0·80604	1·00756	1·20907	1·41058	1·61209	1·81360
0·44444	0.66667	0·88889	1·11111	1·33333	1·55555	1·77778	2·00000
0·60000	0·90000	1·20000	1·50000	1·80000	2·10000	2·40000	2·70000
0·14350	0·21525	0·28700	0·35874	0·43049	0·50224	0·57399	0·64574
0·57143	0·85714	1·14286	1·42857	1·71429	2·00000	2·28571	2·57143
0·79939	1·19909	1·59879	1·99849	2·39818	2·79788	3·19758	3·59727
0·45070	0 67606	0·90141	1·12676	1·35211	1·57746	1·80282	2·02817
0·55895	0·83843	1·11790	1·39738	1·67686	1·95633	2·23581	2·51528
0·60759	0·91139	1·21519	1·51899	1·82278	2·12658	2·43038	2·73417
0·07692	0·11539	0·15385	0·19231	0·23077	0·26923	0·30770	0·34616
0·14815	0·22222	0·29630	0·37037	0·44444	0·51852	0·59259	0·66667
0·42667	0·64000	0·85333	1·06667	1·28000	1·49333	1·70667	1·92000
0·33964	0·50946	0·67928	0·84910	1·01892	1·18874	1·35856	1·52838
1·06667	1·60000	2·13333	2·66667	3·20000	3·73333	4·26667	4·80000
0·13796	0·20694	0·27592	0·34490	0·41388	0·48286	0·55184	0·62082
0·51621	0·77431	1·03242	1·29052	1·54863	1·80673	2·06484	2·32294
0·30918	0·46377	0·61836	0·77295	0·92753	1·08212	1·23671	1·39130
0·42667	0·64000	0·85333	1·06667	1·28000	1·49333	1·70667	1·92000
1·77778	2·66667	3·55556	4·44445	5·33333	6·22222	7·11111	8·00000
0·39480	0·59220	0·78960	0·98700	1·18440	1·38180	1·57920	1·77660
0·87324	1·30986	1·74648	2·18309	2·61971	3·05633	3·49295	3·92957
1·27928	1·91892	2·55856	3·19820	3·83784	4·47748	5·11712	5·75676
0·94040	1·41060	1·88080	2·35099	2·82119	3·29139	3·76159	4·23179
0·33898	0·50847	0·67796	0·84745	1·01694	1·18643	1·35592	1·52541
0·39821	0·59731	0·79641	0·99551	1·19462	1·39372	1·59282	1·79192
0·46874	0·70311	0·93748	1·17185	1·40622	1·64059	1·87496	2·10933
1·66036	2·49054	3·32072	4·15090	4·98108	5·81126	6·64144	7·47162
1·08161	1·62241	2·16321	2·70402	3·24482	3·78563	4·32643	4·86723

TABLE IV.

Elements.	Found.	Sought.	1
Potassium	Chloride of potassium KCl	Potassium K	0·52445
	Chloride of potassium KCl	Potassa KO	0·63173
	Potassio-bichloride of platinum $KCl, PtCl_2$	Potassa KO	0·19272
	Potassio-bichloride of platinum $KCl, PtCl_2$	Chloride of potassium KCl	0·30507
Silicon	Silicic acid SiO_2	Silicon Si	0·46667
Silver	Chloride of silver $AgCl$	Silver Ag	0·75276
	Chloride of silver $AgCl$	Oxide of silver AgO	0·80854
Sodium	Soda NaO	Sodium Na	0·74190
	Sulphate of soda NaO, SO_3	Soda NaO	0·43658
	Chloride of sodium $NaCl$	Soda NaO	0·53022
	Chloride of Sodium $NaCl$	Sodium Na	0·39337
	Carbonate of soda NaO, CO_2	Soda NaO	0·58487
Strontium	Strontia SrO	Strontium Sr	0·84541
	Sulphate of strontia SrO, SO_3	Strontia SrO	0·56403
	Carbonate of strontia SrO, CO_2	Strontia SrO	0·70169
Sulphur	Sulphate of baryta BaO, SO_3	Sulphur S	0·13734
	Tersulphide of arsenic AsS_3	Sulphur S_3	0·39024
	Sulphate of baryta BaO, SO_3	Sulphuric acid SO_3	0·34335
Tin	Binoxide of tin SnO_2	Tin Sn	0·78667
	Binoxide of tin SnO_2	Protoxide of tin SnO	0·89333
Zinc	Oxide of zinc ZnO	Zinc Zn	0·80260
	Sulphide of zinc ZnS	Oxide of zinc ZnO	0·83515
	Sulphide of zinc ZnS	Zinc Zn	0·67031

(*continued*).

2	3	4	5	6	7	8	9
1·04890	1·57335	2·09780	2·62225	3·14669	3·67114	4·19559	4·72004
1·26346	1·89519	2·52692	3·15865	3·79037	4·42210	5·05383	5·68556
0·38545	0·57817	0·77090	0·96362	1·15634	1·34907	1·54179	1·73452
0·61015	0·91522	1·22030	1·52537	1·83044	2·13552	2·44059	2·74567
0·93333	1·40001	1·86667	2·33333	2·80000	3·26667	3·73333	4·20000
1·50552	2·25828	3·01104	3·76380	4·51656	5·26932	6·02208	6·77484
1·61708	2·42562	3·23416	4·04270	4·85124	5·65978	6·46832	7·27686
1·48379	2·22569	2·96758	3·70948	4·45137	5·19327	5·93516	6·67706
0·87316	1·30975	1·74633	2·18291	2·61949	3·05607	3·49265	3·92924
1·06043	1·59065	2·12086	2·65108	3·18130	3·71151	4·24173	4·77194
0·78673	1·18009	1·57346	1·96683	2·36019	2·75356	3·14692	3·54029
1·16974	1·75460	2·33947	2·92434	3·50921	4·09407	4·67894	5·26381
1·69082	2·53623	3·38164	4·22705	5·07247	5·91788	6·76329	7·60870
1·12807	1·69210	2·25613	2·82017	3·38420	3·94823	4·51226	5·07630
1·40339	2·10508	2·80678	3·50848	4·21017	4·91186	5·61356	6·31526
0·27468	0·41202	0·54936	0·68670	0·82403	0·96137	1·09871	1·23605
0·78049	1·17073	1·56097	1·95122	2·34146	2·73170	3·12194	3·51219
0·68670	1·03004	1·37339	1·71674	2·06009	2·40344	2·74678	3·09013
1·57333	2·36000	3·14667	3·93333	4·72000	5·50667	6·29334	7·08000
1·78667	2·68000	3·57333	4·46667	5·36000	6·25333	7·14666	8·04000
1·60520	2·40780	3·21040	4·01300	4·81560	5·61820	6·42080	7·22340
1·67031	2·50546	3·34062	4·17577	5·01092	5·84608	6·68123	7·51639
1·34061	2·01092	2·68123	3·35154	4·02184	4·69215	5·36246	6·03276

TABLE V.

SPECIFIC GRAVITY AND ABSOLUTE WEIGHT OF SEVERAL GASES.

	Specific gravity, atmospheric air = 1·0000.	1 litre (1000 cubic centimetres) of gas at 0° and 0·76 metre bar. pressure weighs grammes.
Atmospheric air	1·0000	1·29366
Oxygen	1·10832	1·43379
Hydrogen	0·06927	0·08961
Water, vapor of	0·62343	0·80651
Carbon, vapor of	0·83124	1·07534
Carbonic acid	1·52394	1·97146
Carbonic oxide	0·96978	1·25456
Marsh gas	0·55416	0·71689
Elayl gas	0·96978	1·25456
Phosphorus, vapor of	4·29474	5·55593
Sulphur, vapor of	6·64992	8·60273
Hydrosulphuric acid	1·17759	1·52340
Iodine, vapor of	8·78898	11·36995
Bromine, vapor of	5·53952	7·16625
Chlorine	2·45631	3·17763
Nitrogen	0·96978	1·25456
Ammonia	0·58879	0·76169
Cyanogen	1·80102	2·32991

TABLE VI.

COMPARISON OF THE DEGREES OF THE MERCURIAL THERMOMETER WITH THOSE OF THE AIR THERMOMETER.

According to MAGNUS.

Degrees of the mercurial thermometer.	Degrees of the air thermometer.
100	100·00
150	148·74
200	197·49
250	245·39
300	294·51
330	320·92

EDITOR'S APPENDIX.

CORRECTION OF THE VOLUME OF GASES.

DR. GIBBS' *method of finding at once the total correction for temperature, pressure, and moisture in absolute determinations of nitrogen, or other gases :—**

"I take a graduated tube, which I fill with mercury, then displace about two-thirds of the mercury with air, and invert the tube into a cistern of mercury. Then I make four or five determinations of the volume of the included (moist) air in the usual manner, and find the volume of the air at 0° and 760^{mm} as a mean of all the determinations. This tube I call the companion tube, and it always hangs in the little room I use for gas analyses. Suppose the volume of (dry) air at 0° and 760^{mm} is 132.35 c.c.

"Now, in making an absolute nitrogen determination I collect the nitrogen moist over mercury in a graduated tube, and then suspend the measuring tube by the side of the companion tube. I then by a cord and pulley bring the level of the mercury in the two tubes to correspond exactly, and then read off the volume of air in the companion tube and the volume of nitrogen in the measuring tube. I ought to have stated that the two tubes hang in the same cistern of mercury. Suppose the volume of air in the companion tube to be 143 c.c.; then the total correction for temperature, pressure and moisture will be $143 - 132{\cdot}35 = 10{\cdot}65$ c.c. The correction for the nitrogen will then be found by Rule of Three. As the observed volume of air in the companion tube is to the observed volume of nitrogen, so is (in this case) 10·65 to the required correction. In this way, when the volume of air in the companion tube is once found, *no further observations of temperature, pressure, or height of mercury above the mercury in the cistern* are necessary. The companion tube lasts for an indefinite time. I have even used it filled with water, without any appreciable change in some weeks, but I prefer mercury. As the two tubes hang side by side, there is never an appreciable difference of temperature. My results are most satisfactory. Williamson & Russell have, as you know, used a companion tube for *equating pressures*, but not for finding the total value of the temperature and pressure correction at once; and I believe that my process is wholly new. Certainly it is wonderfully convenient, and saves all tables and labor of computation."

ASSAY OF CHROMIC IRON.

Mix the pulverized ore in a platinum vessel with three parts of pulverized and pure cryolite; upon the top of the mixture place twelve parts of bisulphate of potassa, or of soda; heat, cautiously at first, to fusion, for fifteen minutes; digest the cold fused mass with a little strong hydrochloric acid, for ten minutes—(so far GIBBS and CLARKE, *Am. Jour. Sci.*, 2d ser., xlv., 178); add a few drops of alcohol to reduce any chromic acid; dilute with water, and add cautiously chloride of barium until all sulphuric acid is precipitated. Filter: concentrate the filtrate to a small bulk in a porcelain capsule; add (according to STORER and PEARSON, *Am. Jour. Sci.*, 2d ser., xlviii., pp. 198–200) nitric acid and crystals of chlorate of potash, and maintain the heat (covering the capsule with an inverted funnel) until the chromium is all oxidized to chromic acid; add, if needful, more chloride of barium, to convert the chromic acid into chromate of barium; evaporate off the great excess of acid; dilute. Allow the precipitate to subside; decant the clear liquid into a filter; wash the precipitate by decantation with solution of acetate of ammonia, finally transferring it to the filter; dry; ignite gently apart from the filter, and weigh the chromate of baryta.

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* Private communication.

NOTE.—The above scheme, as yet untried by the Editor, is simply proposed as an attempt to combine the best points in the two valuable communications referred to, with a view to make a rapid method for estimating chromium in its ore. The observation of Storer and Pearson in the paper above cited (p. 200, paragraph v.), promises a still better method, which deserves elaboration.

SEPARATION OF PHOSPHORIC ACID FROM LIME, ALUMINA, AND OXIDE OF LIME.

In absence of *sulphuric acid*, BRASSIER (*Ann. Chim. Phys.* [4] vii., 355) dissolves the phosphates in hydrochloric acid, adds ammonia in excess, and re-dissolves the precipitated phosphates by additions of citric acid, keeping the liquid ammoniacal. From the solution thus obtained, the phosphoric acid is thrown down by chloride of magnesium, as pure ammonio-magnesian phosphate. Since the latter is sensibly soluble in citrate of ammonia, the citric acid solution should be added, drop by drop, avoiding an excess. The chloride of magnesium should be free from sulphuric acid, otherwise sulphate of lime would also be precipitated. It is to be expected that the results will fall out too low in presence of much iron or alumina (see p. 276, α), but the method is very convenient for the analysis of bone-black and many native phosphates.

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